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DOCKET NO.: B1029.70001US00

ARG

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent No.:	6,776,932 B1
Issue Date:	August 17, 2004
Applicant:	Victor M. Ilyashenko
Serial No.:	09/445,733
Confirmation No.:	1310
Filed:	August 29, 2000
For:	POLYMERIC OPTICAL ARTICLES
Examiner:	Mathieu D. Vargot
Art Unit:	1732

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

The undersigned hereby certifies that this document is being placed in the United States mail with first-class postage attached, addressed to Certificate of Correction Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on the 21 day of June, 2005.

Maureen Joyce

Certificate of Correction Branch
Commissioner For Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Certificate
JUN 3 0 2005
of Correction

Sir:

Transmitted herewith are the following documents:

- Supplemental Request for Certificate of Correction Under 37 C.F.R. §1.323
- Certificate of Correction
- Copy of Transmittal Letter to the United States Receiving Office Dated June 12, 1998 (Attorney Docket No.: B1029.70001WO00)
- Document Comparing the Written Texts of U.S. Patent Application Serial No.: 08/873,952 as filed and International Application No.: PCT/US98/12295 as filed
- Return Receipt Postcard

If the enclosed papers are considered incomplete, the Mail Room and/or the Application Branch is respectfully requested to contact the undersigned at (617) 646-8000, Boston, Massachusetts.

A check is not enclosed. If a fee is required, the Commissioner is hereby authorized to charge Deposit Account No. 23/2825.

JUL 0 6 2005

A duplicate of this sheet is enclosed.

Respectfully submitted,

By:

Michael J. Pomianek, Ph.D., Reg. No.: 46,190
Wolf, Greenfield & Sacks, P.C.
600 Atlantic Avenue
Boston, Massachusetts 02210-2206
Telephone: (617) 646-8000

Docket No.: B1029.70001US00
Date: June 21, 2005
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JUN 23 2005
PATENT & TRADEMARK OFFICE

Attorney's Docket No.: B1029.70001US00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent No.	:	6,776,932 B1
Issue Date	:	August 17, 2004
Applicants	:	Victor M. Ilyashenko
Filing Date	:	August 29, 2000
For	:	POLYMERIC OPTICAL ARTICLES
Examiner	:	Mathieu D. Vargot
Art Unit	:	1732
Conf. No.	:	1310

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8(a)

The undersigned hereby certifies that this document is being placed in the United States mail with first-class postage attached addressed to the Certificate of Correction Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on June 21, 2005.

Maureen Jorge

Certificate of Correction Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

SUPPLEMENTAL REQUEST FOR CERTIFICATE OF CORRECTION UNDER 37 C.F.R. §1.323

Dear Sir:

Applicant submits herewith a Supplemental Request for Certificate of Correction under 37 C.F.R. §1.323 to correct an incorrect reference to a prior co-pending application in the priority claim language in column 1, lines 11-19 of the above-identified issued patent, which corrections do not constitute new matter or require re-examination.

Applicant previously submitted a Request for Certificate of Correction under 37 C.F.R. §1.323 on September 15, 2004 for the above-identified issued patent requesting that in Column 1, Line 14, the text be corrected to read "is a continuation-in-part of" instead of "claims priority to" as printed. On May 24, 2005, the Patent Office issued a Certificate of Correction; however, the correction substituted "is a continuation of" for "claims priority to" instead of substituting "is a continuation-in-part of" for "claims priority to" as Applicant requested.

Applicant believes that the previous submission in support of the issued Request for Certificate of Correction under 37 C.F.R. §1.323 may have inadvertently created confusion as to whether the above-identified issued patent is properly a continuation of or a continuation-in-part of U.S. Patent Application Serial No. 08/873,952 (now U.S. Patent No. 6,086,999). Specifically, it is

noted that on the copy provided of the Transmittal Letter submitted to the United States Receiving Office with International Application No. PCT/US98/12295 upon filing of the International Application, which is also included as part of the present submission, in item II.D, the box indicating that the International Application "is identical to" U.S. Patent Application Serial No. 08/873,952 was checked. This was an inadvertent error made in good faith without deceptive intent. Instead, the box adjacent to item II.E should have been checked, indicating that the International Application "contains additional subject matter not found in [U.S. Patent Application Serial No. 08/873,952]." It is readily apparent upon reviewing the text of U.S. Patent Application Serial No. 08/873,952 as filed and International Application No. PCT/US98/12295 as filed that the specifications are not identical and that additional text was included in International Application No. PCT/US98/12295. Accordingly, it is believed that it is clear from the Patent Office Record that the proper relationship of International Application No. PCT/US98/12295 to U.S. Patent Application Serial No. 08/873,952 is as a continuation-in-part. In support, as indicated below, Applicant includes as part of the present submission a document comparing the written texts of U.S. Patent Application Serial No. 08/873,952 as filed and International Application No. PCT/US98/12295 as filed illustrating changes.

Summarizing the basis and support for the present Supplemental Request for Certificate of Correction under 37 C.F.R. §1.323, Applicant inadvertently did not properly indicate the relationship between International Application No. PCT/US98/12295, of which the instant patent was granted on a national stage filing thereof, and U.S. Patent Application Serial No. 08/873,952 (now U.S. Patent No. 6,086,999) to which the International Application claimed the benefit of priority. The priority claim should have recited that International Application No. PCT/US98/12295 is a <u>continuation-in-part</u> of U.S. Patent Application Serial No. 08/873,952, now U.S. Patent No. 6,086,999. The attached certificate of correction effects this correction. The mistake was made in good faith.

Applicants note that the instant application was granted on an application filed prior to November 29, 2000, and that, therefore, the version of 37 C.F.R. §1.78 in effect as of November 29, 2000 applies. Applicants further note that all of the requirements set forth in the version of 37

C.F.R. §1.78(a)(1) in effect as of November 29, 2000 have been met in the application that matured into the instant patent to be corrected. In addition, it is clear from the record of the patent and patent application that the indicated priority is appropriate. As evidence, Applicant includes herewith a copy of:

(1) copies of the Transmittal Letter (mistakenly indicating that International Application No. PCT/US98/12295 "is identical to" U.S. Patent Application Serial No. 08/873,952 instead of indicating that the International Application "contains additional subject matter not found in [U.S. Patent Application Serial No. 08/873,952]" –see discussion above) and PCT Request form submitted to the United States Receiving Office with International Application No. PCT/US98/12295 upon filing, which clearly indicates that the International Application designated the United States of America (page 2 of Request) and claimed priority to U.S. Patent Application Serial No. 08/873,952 (page 3 of Request);

(2) a copy of the Notice of Status of Requirements Under 35 U.S.C. 371 form mailed by the U.S. Patent and Trademark Office upon receipt of the International Application indicating the International Application Number and acknowledging Applicant's priority date claimed (i.e. the 12 June 1997 filing date of U.S. Patent Application Serial No. 08/873,952); and

(3) a document comparing the written texts of U.S. Patent Application Serial No. 08/873,952 as filed and International Application No. PCT/US98/12295 as filed and showing changes with text added in the International Application indicated in double underline and deletions of text present in U.S. Patent Application Serial No. 08/873,952 in strike-through.

It is requested that the undersigned be contacted by telephone call at (617) 720-3500 with any questions relating to this Request.

Please charge any fee or any fee deficiency occasioned by t his Request to Deposit Account No. 23/2825.

Respectfully submitted,

Michael J. Pomianek, Reg. No. 46,190
WOLF, GREENFIELD & SACKS, P.C.
600 Atlantic Avenue
Boston, MA 02210-2211
Tel. (617) 646-8000

Date: June 21, 2005
XNDD 825063.2

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO.	:	6,776,932 B1
DATED	:	August 17, 2004
INVENTOR(S)	:	Victor M. Ilyashenko

It is certified that errors appear in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 1, at line 14, "claims priority to" should read -- is a continuation-in-part of --

MAILING ADDRESS OF SENDER

PATENT NO. 6,776,932 B1

Michael J. Pomianek, Ph.D., Reg. No. 46,190
Wolf, Greenfield & Sacks, P.C.
600 Atlantic Avenue
Boston, Massachusetts 02210

FORM PTO 1050 (Rev. 2-93)
908923

JUL 0 6 2005

TRANSMITTAL LETTER TO THE UNITED STATES RECEIVING OFFICE

Date	12 June 1998 (12.06.98)
International Application No.	
Attorney Docket No.	B1029/7001WO

I. Certification under 37 CFR 1.10 (if applicable)

EM529446915US	12 June 1998 (12.06.98)
Express Mail Mailing Number	Date of Deposit

II. ☒ New International Application

TITLE	POLYMERIC OPTICAL ARTICLES	Earliest priority date (Day/Month/Year): 12 June 1997 (12.06.97)

SCREENING DISCLOSURE INFORMATION: In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied. (Note: check as many boxes as apply):

A. ☐ The invention disclosed was **not** made in the United States.

B. ☐ There is no prior U.S. application relating to this invention.

C. ☒ The following prior U.S. application(s) contain subject matter which is related to the invention disclosed in the attached international application. *(NOTE: priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority.)*

Application No.	08/873,952	filed on	12 June 1997 (12.06.97)
Application No.		filed on	

D. ☒ The present international application ☒ is identical to ☐ contains less subject matter than that found in the prior U.S. application(s) identified in paragraph C above.

E. ☐ The present international application ☐ contains additional subject matter not found in the prior U.S. application(s) identified in paragraph C above. The additional subject matter is found on pages ____ and ☐ **DOES NOT ALTER** ☐ **MIGHT BE CONSIDERED TO ALTER** the general nature of the invention in a manner which would require the U.S. application to have been made available for inspection by the appropriate defense agencies under 35 U.S.C. 181 and 37 CFR 5.1. See 37 CFR 5.15.

III. ☐ **A Response to an Invitation from the RO/US.** The following document(s) is/are enclosed:

A. ☐ A Request for An Extension of Time to File a Response

B. ☐ A Power of Attorney (General or Regular)

C. ☐ Replacement pages:

pages		of the request	pages		of the figures
pages		of the description	pages		of the abstract
pages		of the claims			

D. ☐ Submission of Priority Documents

Priority document		Priority document	

E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☐ **A Request for Rectification under PCT 91** ☐ **A Petition** ☐ **A Sequence Listing Diskette**

V. ☒ **Other (please specify):**

PCT Req. Form RO/101 (3 shts); Fee Calculation Sheet; Application for Patent (23 shts Desc, 10 shts clms, 1 sht Abst, 2 shts drwgs)

The person signing this form is the:		
	☐ Applicant	GATES, Edward R.
		Typed Name of Signer
	☒ Attorney/Agent Reg. No. 31,616	Edward R Gates
	☐ Common Representative	Signature

PTO-1382 (Rev. 4-1995)

U.S. Department of Commerce: Patent and Trademark Office

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For r[illegible]ng Office use only
International Application No.
International Filing Date
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference: **B1029/7001WO**
(if desired) (12 characters maximum)

Box No. I TITLE OF INVENTION
POLYMERIC OPTICAL ARTICLES

Box No. II APPLICANT

Name and address: *(Family name, followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)*

BOSTON OPTICAL FIBER, INC.
155 Flanders Road
Westborough, Massachusetts 01581
United States of America

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State *(i.e., country)* of nationality: **US**

State *(i.e., country)* of residence: **US**

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name, followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (i.e. country) of residence if no State of residence is indicated below.)*

ILYASHENKO, Victor M.
3122 Arbor Drive
Shrewsbury, Massachusetts 01545
United States of America

This person is:
☐ applicant only
☒ applicant and inventor
☐ inventor only *(if this check-box is marked, do not fill in below.)*

State *(i.e., country)* of nationality: **US**

State *(i.e., country)* of residence: **RU**

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name, followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

GATES, Edward R.
Wolf, Greenfield & Sacks, P.C.
600 Atlantic Avenue
Boston, Massachusetts 02210
United States of America

Telephone No.
617 720-3500

Facsimile No.
617 720-2441

Teleprinter No.

☐ Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. V **DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes; at least one must be marked)*:

Regional Patent

- [X] **AP** **ARIPO Patent:** **GH** Ghana, **GM** Gambia, **KE** Kenya, **LS** Lesotho, **MW** Malawi, **SD** Sudan, **SZ** Swaziland, **UG** Uganda, **ZW** Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- [X] **EA** **Eurasian Patent:** **AM** Armenia, **AZ** Azerbaijan, **BY** Belarus, **KG** Kyrgyzstan, **KZ** Kazakhstan, **MD** Republic of Moldova, **RU** Russian Federation, **TJ** Tajikistan, **TM** Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- [X] **EP** **European Patent:** **AT** Austria, **BE** Belgium, **CH and LI** Switzerland and Liechtenstein, **DE** Germany, **DK** Denmark, **ES** Spain, **FI** Finland, **FR** France, **GB** United Kingdom, **GR** Greece, **IE** Ireland, **IT** Italy, **LU** Luxembourg, **MC** Monaco, **NL** Netherlands, **PT** Portugal, **SE** Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- [X] **OA** **OAPI Patent:** **BF** Burkina Faso, **BJ** Benin, **CF** Central African Republic, **CG** Congo, **CI** Côte d'Ivoire, **CM** Cameroon, **GA** Gabon, **GN** Guinea, **ML** Mali, **MR** Mauritania, **NE** Niger, **SN** Senegal, **TD** Chad, **TG** Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment is desired, specify on dotted line)* ....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

- [X] **AL** Albania ....
- [X] **AM** Armenia ....
- [X] **AT** Austria ....
- [X] **AU** Australia ....
- [X] **AZ** Azerbaijan
- [X] **BA** Bosnia and Herzegovina ....
- [X] **BB** Barbados
- [X] **BG** Bulgaria ....
- [X] **BR** Brazil ....
- [X] **BY** Belarus
- [X] **CA** Canada
- [X] **CH and LI** Switzerland and Lichtenstein
- [X] **CN** China ....
- [X] **CU** Cuba ....
- [X] **CZ** Czech Republic ....
- [X] **DE** Germany ....
- [X] **DK** Denmark ....
- [X] **EE** Estonia ....
- [X] **ES** Spain ....
- [X] **FI** Finland ....
- [X] **GB** United Kingdom
- [X] **GE** Georgia ....
- [X] **GH** Ghana ....
- [X] **GM** Gambia
- [X] **GW** Guinea-Bissau..........
- [X] **HU** Hungary ....
- [X] **ID** Indonesia ....
- [X] **IL** Israel ....
- [X] **IS** Iceland
- [X] **JP** Japan ....
- [X] **KE** Kenya ....
- [X] **KG** Kyrgyzstan ....
- [X] **KP** Democratic People's Republic of Korea ....
- [X] **KR** Republic of Korea ....
- [X] **KZ** Kazakhstan ....
- [X] **LC** Saint Lucia
- [X] **LK** Sri Lanka
- [X] **LR** Liberia
- [X] **LS** Lesotho ....
- [X] **LT** Lithuania
- [X] **LU** Luxembourg ....
- [X] **LV** Latvia
- [X] **MD** Republic of Moldova ....
- [X] **MG** Madagascar ....
- [X] **MK** The former Yugoslav Republic of Macedonia ....
- [X] **MN** Mongolia
- [X] **MW** Malawi ....
- [X] **MX** Mexico ....
- [X] **NO** Norway
- [X] **NZ** New Zealand ....
- [X] **PL** Poland ....
- [X] **PT** Portugal ....
- [X] **RO** Romania
- [X] **RU** Russian Federation ....
- [X] **SD** Sudan
- [X] **SE** Sweden
- [X] **SG** Singapore
- [X] **SI** Slovenia ....
- [X] **SK** Slovakia ....
- [X] **SL** Sierra Leone
- [X] **TJ** Tajikistan ....
- [X] **TM** Turkmenistan ....
- [X] **TR** Turkey ....
- [X] **TT** Trinidad and Tobago ....
- [X] **UA** Ukraine ....
- [X] **UG** Uganda ....
- [X] **US** United States of America ....
- [X] **UZ** Uzbekistan ....
- [X] **VN** Viet Nam ....
- [X] **YU** Yugoslavia ....
- [X] **ZW** Zimbabwe

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- [X] All States party to PCT as of International Filing Date
- [ ]
- [ ]

In addition to the designations made above, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except the designation(s) of ____________

The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)*

Box No. VI **PRIORITY CLAIM** Further priority claims are indicated in Supplemental Box ☐

The priority of the following earlier application(s) is hereby claimed:

Country *(in which, or for which, the application was filed)*	Filing Date *(day/month/year)*	Application No.	Office of filing *(only for regional or international application)*
item (1) US	**12 June 1997 (12.06.97)**	**08/873,952**	
item (2)			
item (3)			

Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):

☒ The receiving Office is hereby requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s): (1)

Box No. VII **INTERNATIONAL SEARCHING AUTHORITY**

Choice of International Searching Authority (ISA) *(If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):* ISA / EP

Earlier search *Fill in where a search (international, international-type or other) by the International Searching Authority has already been carried out or requested and the Authority is now requested to base the international search, to the extent possible, on the results of that earlier search. Identify such search or request either by reference to the relevant application (or the translation thereof) or by reference to the search request.*

Country (or regional Office): Date *(day/month/year)*: Number:

Box No. VIII **CHECK LIST**

This international application contains the following number of sheets:

1. request :	03	sheets
2. description:	23	sheets
3. claims :	10	sheets
4. abstract :	01	sheets
5. drawings:	02	sheets
TOTAL	39	

This international application is accompanied by the item(s) marked below:

1. ☐ separate signed power of attorney
2. ☐ copy of general power of attorney
3. ☐ statement explaining lack of signature
4. ☐ priority document(s) *identified in Box No. VI as item(s):*
5. ☒ fee calculation sheet
6. ☐ separate indications concerning deposited microorganisms
7. ☐ nucleotide and/or amino acid sequence listing (diskette)
8. ☒ other *(specify)*: **postcard, transmittal letter k**

Figure No. 1 of the drawings (if any) should accompany the abstract when it is published.

Box No. IX **SIGNATURE OF APPLICANT**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Edward R Gates

GATES, Edward R.

For receiving Office use only

1. Date of actual receipt of the purported international application:
2. Drawings
   ☐ received
   ☐ not received
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:
4. Date of timely receipt of the required corrections under PCT Article 11(2)
5. International Searching Authority specified by the applicant: ISA /
6. ☐ Transmittal of search copy delayed until search fee is paid

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

TO

EDWARD R. GATES
WOLF, GREENFIELD & SACKS, P.C.
600 ATLANTIC AVENUE
BOSTON MA 02210

DOCKETED
JUL 15 1998

File Folder
Electronic Code Book
Docket Entry 2-12-99
Docket Cross Off
Order Copies
Annuities 12-12
Other

UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

NOTIFICATION OF STATUS OF REQUIREMENTS UNDER 35 U.S.C.371

DATE OF MAILING	JUL 14 1998
FILE REFERENCE	B1029/7001WO

IDENTIFICATION OF INTERNATIONAL APPLICATION

International Application Number	International Filing Date	Priority Date Claimed
PCT/US98/12295	12 JUN 98	12 JUN 97

Applicant for DO/EO/US

BOSTON OPTICAL FIBER, INC.

NOTIFICATION

The applicant is hereby advised that the U.S. Patent and Trademark Office in its capacity as ☐ Designated Office ☐ Elected Office has received the following items as of the date of mailing indicated above.

1. ☐ U.S. National fee [35 U.S.C.371 (c) (1)]
2. ☐ Oath of declaration [35 U.S.C.371 (c) (4)]
3. ☒ Copy of International application as filed [35 U.S.C.371 (c) (2)]
4. ☐ Translation of Application [35 U.S.C.371 (c) (2)]
5. ☐ Amendments under PCT Article 19 [35 U.S.C.371 (c) (3)
6. ☐ Translation of PCT Article 19 Amendments [35 U.S.C.371 (c) (3)
7. ☐ Search Report or Declaration under PCT Article 17(2) [35 U.S.C.371 (a)]
8. ☐ International Preliminary Examination Report and its Annexes, if any, under PCT Article 36(3) (a) [35 U.S.C.371 (a)]
9. ☐ Translation of Annexes to the International Preliminary Examination Report under PCT Article 36(3) (b) [35 U.S.C.371 (c) (5)]
10. ☐ Other items received:
    ☐ Assignment Document ☐ Prior Art Statement ☐ Preliminary Amendment

A. ☐ Requirements for U.S. National processing have been met. Processing will commence
  ☐ at the expiration of the applicable time limit under either
    ☐ PCT Article 22 [35 U.S.C.371 (b)] or
    ☐ PCT Article 39 [35 U.S.C.371 (b)]
  ☐ on the date indicated below under the provisions of 35 U.S.C.371 (f)

U.S. NATIONAL SERIAL#	DATE UNDER 35 U.S.C.102(e)	DATE OF COMMENCEMENT OF NATIONAL PROCESSING

All correspondence submitted after the date of commencement of U.S. National processing indicated above should refer to the U.S. National Serial Number and the appropriate U.S. National processing organization or Officer.

B. ☐ As the above identified application has been accepted for U.S. National processing under the provisions of 35 U.S.C.371 (f) before expiration of the applicable time limit under ☐ PCT Article 22 ☐ PCT Article 39, applicant is reminded that
  ☐ Amendments under PCT Article 19 and/or
  ☐ the International Preliminary Examination Report and its Annexes, if any, under PCT Article 36(3) (a), and (b)
and any translation thereof, if applicable, must be submitted to the Patent and Trademark Office as soon as they are available.

INTERNATIONAL APPLICATION NUMBER	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US98/12295	12 JUN 98	12 JUN 97

C. [x] In order that U.S. National processing may begin, certain items must be received by the DO/EO/US by the expiration of the applicable time-limit under

- [ ] PCT Article 22 or
- [ ] PCT Article 39.

Specifically:

- [x] 1. U.S. National Fee
- [x] 2. Oath or Declaration
- [ ] 3. Copy of Application
- [ ] 4. Translation of Application
- [x] 5. Amendments under PCT Article 19, if any
- [ ] 6. Translation of PCT Article 19 Amendments, if applicable
- [ ] 7. Search Report or PCT Article 17(2)(a) declaration
- [ ] 8. International Preliminary Examination Report and its Annexes, if any, under PCT Article 36(3)(a), if applicable
- [ ] 9. Translation of Annexes to the International Preliminary Examination Report under PCT Article 36(3)(b), if applicable

THE ABOVE CHECKED ITEMS MUST BE TIMELY RECEIVED TO AVOID ABANDONMENT OF THE APPLICATION. [35 U.S.C.371(d)]

D. Further information for the applicant:

THE ABOVE IDENTIFIED ITEMS ARE NEEDED FOR ENTRY INTO THE NATIONAL STAGE

A REMINDER ONLY

UNITED STATES DESIGNATED/ELECTED OFFICE

Address Only:	Authorized Officer
Commissioner of Patents and Trademarks Box PCT Washington D.C. 20231 ATTN: DO/EO/US	Hal Arundine

Document Comparing the Written Texts of U.S. Patent Application Serial No. 08/873,952 as filed and International Application No. PCT/US98/12295 as filed.

~~t'.)F-''-01 .APL~~[1] POLYMERIC OPTICAL ARTICLES[2]
~~L>1 1A0 9~~[3]
~~AOC/SMA/kdq 06/12/97~~[4]
~~PATENT APPLICATION~~[5]

~~Date: June /12 /1997~~[6]
~~EXPRESS MAIL LABEL NO. EG9788~~[7]

~~-1-~~[8]

~~Inventor:~~[9] This application claims priority to U.S. Ser. No. 08/873,952, entitled "Method for Producing a Graded Index Plastic Optical Material," filed June 12, 1997, by[10] Victor M. Ilyashenko ~~Attorney's Docket No.: BOF97-01~~[11] .[12]

~~METHOD FOR PRODUCING A GRADED INDEX~~[13]
~~PLASTIC OPTICAL MATERIAL~~[14]

GOVERNMENT FUNDING

The invention described herein was made in whole or in part with government support under a contract issued by the Defense Advanced Research Projects Agency (DARPA) in response to DARPA solicitation #BAA96-29 and under contract number DAA20L-94-C-3425 with the Defense [15]Advanced Research

Projects Agency (~~ARPA~~[16]DARPA[17]). The United States Government may have certain rights in the invention.

BACKGROUND OF THE INVENTION

Optical resin materials which are characterized by a distributed refractive index have ~~demonstrated usefulness~~[18]proved useful[19] in the construction of optical conductors such as, optical fibers, optical waveguides, ~~and~~[20]optical integrated circuits~~as well as~~[21], and[22] the corresponding preforms ~~of~~[23]from which[24] these optical [25]conductors are fabricated[26]. In general, plastic or polymeric [27]optical fibers (POF) are considered an attractive alternative to copper cable and glass optical fibers. Typically, the plastic optical fiber (or thin, flexible optical [28]rod) has ~~a~~[29]an elongated[30] core within which the majority of the [31]light travels in a generally axial direction [32]and a sheathing layer which coaxially [33]surrounds the core~~,~~[34] and[35] confines the

~~2~~[36] light to the core ~~and possesses~~[37]due to its having[38] an index of refraction less than that of the core.

The refractive index distribution of plastic optical fibers can be classified as either a [39]gradient (or graded) [40]index or step index. However, ~~graded~~[41]gradient[42] index plastic optical fibers (GI POF) are preferred over step index fibers for many [43]data communication applications~~. That is, the~~[44] due to their superior bandwidth capacity. The[45] index of refraction~~,~~[46] in a ~~graded~~[47]gradient[48] index plastic optical fiber has a distribution that continuously changes within the core of the[49] fiber, generally ~~decreases~~[50]decreasing[51] radially from a maximum value at [52]the core ~~center outward~~[53]central axis outwardly [54]until it ~~matches~~[55]approaches the lower index of refraction of[56] the sheathing ~~index~~[57]at or near[58] the core-sheathing interface. ~~Therefore,~~[59]Due to this continuously varying refractive index within the core, the optical fiber acts like a lens tending to refocus light rays, reducing their propagation in non-axial directions, so that[60] light rays entering the core at a small angle, with respect to the axis, follow undulating paths~~, which is not the case for~~[61] with relatively small deviations from the axial direction when compared to light propagation in[62] a step index type fiber. ~~The~~[63]In addition, the[64] speed of the light rays ~~along the~~[65]following[66] undulating paths~~increases~~[67] is higher[68] in the regions of lower refractive index so that the total [69]travel time ~~along these~~[70]for light rays following undulating[71] paths is nearly equal to ~~that along the~~[72]those following a[73] straight axial path. This results in, for example, a fiber with a [74]wider bandwidth of transmission with minimal modal dispersion and a more rapid information flow than that obtained with step index plastic optical fibers.

In general, typical [75]methods of fabricating ~~graded~~[76]gradient[77] index plastic optical ~~materials comprise~~[78]fibers involve[79] preparation of a polymeric sheathing and a polymeric core disposed within the sheathing~~.~~[80] in a coaxial configuration. [81] The refractive index of the core and sheathing are different ~~in that~~[82]and, for most optical conducting applications,[83] the refractive index of the core is greater than that of the sheathing. Frequently, the core is made of

[84]the same polymer as that which comprises the sheathing but, in addition, further[85] includes a non-polymeric substance (commonly referred to as a dopant) which ~~causes~~[86]increases [87]the refractive index of the core ~~to be~~[88]so that it is[89] greater than that of the sheathing. ([90]See for example, U.S. Patent No. 5,541,247 to Koike.)[91]

However, currently available methods of fabrication have significant shortcomings. For example, the type and ~~35-~~[92]amount of dopant [93]substances which can be incorporated into the

~~-3~~[94] core and still provide a ~~graded~~[95]gradient[96] index plastic optical ~~material~~[97]article[98] which maintains both sufficient optical [99]transparency and an acceptable difference in the refractive index between the sheathing and the core, are limited. Therefore, a need exists for methods and materials useful for fabricating ~~graded~~[100]improved gradient[101] index plastic optical ~~materials~~[102]articles[103].

SUMMARY OF THE INVENTION

~~The~~[104] One aspect of the[105] present invention is based upon the discovery that~~, surprisingly,~~[106] a ~~graded~~[107]gradient[108] index plastic optical ~~material~~[109]article [110]having excellent optical characteristics can be ~~achieved~~[111]produced[112] using a method of ~~manufacturing, which~~[113]fabrication that[114] incorporates a low refractive index dopant (i.e.~~,~~[115] having a refractive index[116] lower than that of [117]the polymer ~~of~~[118]comprising[119] the sheathing but without the dopant[120]) in the sheathing of the ~~material~~[121]article[122].

The present invention ~~thus~~[123]in another aspect[124] relates to a ~~graded~~[125]gradient[126] index plastic optical ~~material~~[127]article[128], and methods of processing the ~~material.~~[129]article. [130] The ~~method~~[131]methods[132] of the invention ~~provides~~[133]provide[134] for the use of a significantly broader selection of dopant and polymeric [135]materials which ~~consequently provides a graded~~[136]can be used to produce a functional gradient[137] index plastic optical ~~fiber~~[138]article[139] with excellent optical characteristics. For example, the~~method~~[140] methods[141] of the invention ~~allows~~[142]allow for[143] control of the ~~graded~~[144]gradient[145] refractive index of the material and ~~thereby produces a graded~~[146]for a wider range of differences in refractive indicies between the core and sheathing for a given concentration of core dopant thereby producing a gradient[147] index plastic optical ~~material~~[148]article[149] with a low loss due to light attenuation[150] and broad transmission bandwidth, having a high level of transparency, a substantial absence of bubbles and good environmental stability, for example, enhanced thermal stability and resistance to humidity.

~~A~~[151]One[152] method for forming a ~~graded~~[153]gradient[154] index plastic optical ~~material~~[155]article according to the invention[156] comprises the steps of: (a) ~~providing~~[157]forming[158] a transparent tube of sheathing material ~~comprising a~~[159]including at least one [160]sheathing polymer and ~~a~~[161]at least one[162] sheathing dopant; and (b) forming a transparent core within the sheathing tube produced in step (a) by: (i) filling the interior space of the sheathing tube~~,~~[163] with a core solution ~~comprising a core~~[164]including at least one[165] polymerizable core[166] monomer which upon polymerization has a refractive index

~~4~~[167] greater than that of the sheathing tube; and ~~(~~[168]ii) allowing the ~~core~~ [169]polymerizable core[170] monomer to polymerize thereby forming a ~~polymer~~[171]polymeric core[172] having a refractive index greater than that of the sheathing tube such that the ~~material~~[173]article[174] is suitable to conduct light~~.~~[175] at at least one wavelength with an attenuation less than 500 dB/km. [176] The core solution can ~~comprise~~[177]include[178] an optional core dopant. When present, the core dopant will have a refractive index greater than that of the polymer obtained upon polymerization of ~~the~~[179]a[180] core monomer~~.~~[181] solution polymerized under the same conditions but not including the core dopant. [182] The product thus obtained, is a ~~graded~~[183]gradient[184] index plastic optical ~~material~~[185]article[186] having an outer ~~transparent~~ [187]sheathing and an inner core both at least partially [188]transparent ~~core.~~[189]to light at at least one wavelength. [190] The refractive index of the central axis of the [191]core ~~is~~[192]will be[193] greater than that of the sheathing such that the ~~material~~[194]article[195] is suitable to conduct light at at least one wavelength with an attenuation less than about 500 dB/km[196], with the refractive index of the core preferably[197] gradually decreasing in a radial direction from the ~~center~~[198]central axis[199] of the core to the periphery~~.~~[200] of the core at the core-sheathing interface. In[201] general, the ~~material~~[202]article[203] is fabricated[204] in the shape of a preform rod. Preferably, the preform rod has a cylindrical shape which can be drawn into fibers.

In ~~a preferred~~[205]one[206] embodiment, the sheathing tube is made by extrusion methods. Alternatively, the sheathing tube can be produced by: (a) placing into a polymerization container a sheathing solution ~~comprising a~~[207]including at least one[208] sheathing polymerizable monomer and ~~a~~[209]at least one[210] sheathing dopant, the sheathing dopant having a refractive index lower than that of the polymer obtained by the polymerization of ~~the~~[211]a[212] sheathing monomer solution under the same conditions but not including the sheathing dopant[213]; and (b) causing the sheathing monomer of the sheathing solution to polymerize within the polymerization container ~~in~~[214]into[215] a cylindrical ~~configuration to form a transparent~~ [216]sheathing tube~~.~~[217] at least partially transparent to light at at least one wavelength. [218]The invention further provides a method for forming a ~~graded~~[219]gradient[220] index plastic optical fiber. ~~The graded~~[221]In the method, the gradient[222] index plastic optical ~~material~~[223]article[224] is prepared, for example~~,~~[225] as described above, in the shape of a preform rod which ~~can~~[226]is[227] then be subjected to hot-drawing at a ~~temperature and speed~~[228]

~~5~~[229]~~suitable to render the fiber useful as an optical conductor.~~[230]predetermined temperature and speed suitable to produce a fiber useful as an optical conductor. In one embodiment, the monomer of the sheathing solution and the monomer of the core solution are the same. Suitable monomers include those which form polymers that are substantially amorphous and capable of conducting light at the desired wavelength(s). For embodiments where the core polymer and the sheathing polymer are the same, when a core dopant is used it will be different from the sheathing dopant. [231]

In another aspect gradient index plastic optical articles of the invention comprise: (a) a polymeric sheathing that is at least partially transparent to light at at least one wavelength including at least one sheathing polymer and at

least one sheathing dopant, where the sheathing dopant has a refractive index which is less than that of the sheathing polymer; and (b) a polymeric core, coaxially disposed within the sheathing, including at least one core polymer and having a refractive index at the central axis of the core greater than that of the polymeric sheathing. In some embodiments, the polymeric core further includes at least one core dopant, the core dopant, when present, having a refractive index which is greater than that of the core polymer. In preferred embodiments, the core dopant has a concentration gradient in a specific direction.[232]

In ~~a certain embodiment, the monomer of the sheathing solution and the monomer of the core solution are the same.~~[233] ~~Suitable monomers include those which form polymers that are substantially amorphous and capable of conducting light in the desired wavelength. In this embodiment, when a core dopant is used it will be different from the sheathing dopant.~~[234]

~~The graded index plastic optical material of the invention comprises (a) a transparent sheathing comprising a sheathing polymer and a sheathing dopant, wherein~~[235] some embodiments, the plastic optical article is in the shape of a cylindrical preform rod. In other embodiments, the article is in the shape of a cylindrical fiber having an outer diameter preferably between about 0.1 millimeter and about 1 millimeter.[236]

In yet another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer and a sheathing dopant, where[237] the sheathing dopant has a refractive index which is less than that of ~~the sheathing polymer; and (b) a transparent core,~~[238]
an equivalent polymeric sheathing without the sheathing dopant. The polymeric core of the article is coaxially [239]disposed within the sheathing, ~~comprising a core polymer having a refractive index greater than that of the sheathing and an optional core dopant, the core dopant, when present, having a refractive index which is greater than that of the core polymer; wherein the core dopant has~~[240] ~~a concentration gradient in a specific direction. The refractive index of the core is greater than that of the doped sheathing.~~[241]
~~In a preferred embodiment, the material is in the~~[242]
~~shape of a cylindrical preform rod. In another application~~[243] ~~the material is in the shape of a cylindrical fiber having an outer diameter between about 0.2 millimeters and about 1 millimeter.~~[244] is at least partially transparent to at least one wavelength of light and includes a core polymer. The polymeric core also has a gradient in refractive index in a specific direction.[245]

In another aspect, the invention provides a method for forming a gradient index plastic optical article. The method involves forming a tube of polymeric sheathing material that is at least partially transparent to at least one wavelength of light from at least one polymerizable sheathing monomer and a sheathing dopant. A polymeric core that is at least partially transparent to at least one wavelength of light is then formed within the tube by filling the tube with a composition including at least one polymerizable core monomer and polymerizing the monomer. The polymeric core thus formed has a gradient in refractive index in a specific direction.[246]

The invention also involves a gradient index plastic optical article which has a polymeric sheathing that includes a sheathing dopant.[247]

In another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric

sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a specific overall concentration of a core dopant that has a refractive index greater than that of the core polymer. Furthermore, the core dopant has a concentration gradient within the core in a specific direction. The polymeric sheathing of the article is constructed and arranged so that the difference in refractive indices between the central axis of the polymeric core and the polymeric sheathing exceeds the difference in refractive indices between the central axis of the polymeric core and the sheathing polymer.[248]

In one aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The core dopant is present in the polymeric core at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value. In addition, the core dopant has a concentration gradient within the core in a specific direction. The polymeric sheathing of the article is constructed and arranged so that the maximum service temperature of the article exceeds that of an equivalent article except having a sheathing comprised of only sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to the same desired value. In general, this increase in the permissible service temperature for articles manufactured according to the present invention having a particular difference in refractive indices between core and sheathing is enabled by the ability to use a lower amount of core dopant in order to create the desired difference in refractive indices.[249]

In yet another aspect, the invention involves a gradient index plastic optical article with a polymeric sheathing and a polymeric core. The polymeric sheathing is at least partially transparent to at least one wavelength of light and includes a sheathing polymer. The polymeric core of the article is coaxially disposed within the sheathing, is at least partially transparent to at least one wavelength of light and includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The core dopant is present in the polymeric core at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value. Furthermore, the core dopant has a concentration gradient within the core in a specific direction. The polymeric sheathing of the article is constructed and arranged so that at least one wavelength of light is conducted by the article with less attenuation than by an equivalent article except having a sheathing comprised of only sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to the same desired value.[250]

In one aspect, the invention involves an optical preform article. The preform includes a polymeric sheathing, which is at least partially transparent to at least one wavelength of light and has a refractive index of a first value at that wavelength. The polymeric sheathing includes a sheathing polymer and a plasticizer. The preform also includes a polymeric core, which includes a core polymer, that is coaxially disposed within the sheathing and is at least

partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis of the core at that wavelength. The preform is fabricated so that the second value of refractive index (i.e. at the central axis of the polymeric core) exceeds the first value (i.e. of the sheathing).[251]

In another aspect, the invention involves a method for making a plurality of optical preform articles. The method involves forming a plurality of polymeric sheathings, each of which includes a sheathing polymer, is at least partially transparent to at least one wavelength of light, and has a refractive index of a first value at that wavelength. The method also involves forming a plurality of polymeric cores, each of which includes a core polymer, that is coaxially disposed within the sheathing and is at least partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis at that wavelength that exceeds the first value of the sheathing. The region of contact between the sheathings and the cores thus formed defines a plurality of interfaces, with essentially all of the plurality of interfaces being essentially free of visible bubbles. In other words, the invention enables a large number of preforms to be made, each of which is essentially free of visible bubbles along its entire "as polymerized" length (e.g. without cutting the preform after polymerization).[252]

In another embodiment, the invention involves an optical preform article. The preform includes a polymeric sheathing, which includes a sheathing polymer, that is at least partially transparent to at least one wavelength of light and has a refractive index of a first value at that wavelength. The preform also includes a polymeric core that is coaxially disposed within the sheathing and is at least partially transparent to the same wavelength(s) of light as the polymeric sheathing, and which has a refractive index of a second value at the central axis of the core at that wavelength that exceeds the first value of the sheathing. The polymeric core includes a core polymer and a core dopant having a refractive index which is greater than that of the core polymer. The core dopant is present in the polymeric core at a specified overall concentration. Furthermore, the second value of refractive index (i.e. of the central axis of the polymeric core) exceeds the first value (i.e. of the polymeric sheathing) by at least 0.01, with the specified overall core dopant concentration not exceeding 12 %wt.[253]

In another aspect, the invention involves a plastic optical article. The article comprises a polymeric sheathing, which is at least partially transparent to at least one wavelength of light and a polymeric core, coaxially disposed within the sheathing, which is also at least partially transparent to the same wavelength of light. The polymeric sheathing includes a sheathing polymer, and the polymeric core includes a core polymer and a core dopant that has a refractive index greater than that of the core polymer. The refractive index of the central axis of the polymeric core has a value at the wavelength of light mentioned above that exceeds the refractive index of the polymeric sheathing at the same wavelength by at least 0.01. Furthermore, the maximum service temperature of the article is at least 40 degrees C, preferably 45 degrees C, and more preferrably 50 degrees C.[254]

In yet another aspect, the invention provides a method for making a gradient plastic optical fiber. The method involves first forming a polymeric preform rod comprising a polymeric sheathing and a polymeric core coaxially disposed within the sheathing that has a gradient in refractive index in a specified direction. The preform is then hot-drawn at a rate of at least 3 m/min, preferably at least 4 m/min, and more preferably, at least 5 m/min, into

a fiber. The fiber thus produced conducts at least one wavelength of light with an attenuation less than 500 dB/km.[255]

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 ~~depicts a preferred~~[256] shows one[257] embodiment of a ~~graded~~[258] gradient[259] index plastic optical ~~material producible by the process of~~[260] article according to[261] the invention~~.~~[262] ;[263]

Figure 2 is a graph showing the relationship between the transmission loss (attenuation)[264] and wavelength of light for[265] an optical fiber~~. The~~[266] according to the invention;[267] transmission~~ loss was measured using standard~~[268]

~~-6~~[269] ~~techniques as described herein. Transmission~~[270] loss at 650 nm was approximately 140 dB/km demonstrating that the optical fiber had a high level of transparency.

DETAILED DESCRIPTION OF THE INVENTION

The features and other details of the invention will now be more particularly described and pointed out ~~below as well as~~[271] in the ~~claims.~~[272] detailed description and examples below.[273] It will be understood that the particular embodiments of the invention are shown by way of illustration only[274] and are[275] not intended to act[276] as limitations of the invention. The principle features of this invention can be employed in various embodiments not specifically described herein[277] without departing from the spirit and[278] scope of the invention.

In one aspect, the invention provides a method for forming a ~~graded~~[279] gradient[280] index plastic optical ~~material comprising~~[281] article including[282] the steps of: (a) forming a ~~transparent tube of sheathing material by:~~[283] tube of polymeric sheathing material that is at least partially transparent to light at at least one wavelength by:[284] (i) placing into a polymerization container a sheathing solution ~~comprising a sheathing polymerizable monomer and a sheathing dopant, wherein the sheathing dopant has a refractive index lower than that of the~~[285] ~~polymer obtained by the polymerization of the sheathing monomer~~[286] including at least one polymerizable sheathing monomer and a plasticizer and/or dopant[287]; and (ii) causing the sheathing monomer of the sheathing solution to polymerize within the polymerization container to ~~give an inner cylindrical configuration in the form of a transparent sheathing tube; and (b) forming a~~[288] ~~transparent core~~[289] form a polymeric sheathing tube at least partially transparent to light at at least one wavelength; and (b) forming a polymeric core coaxially disposed[290] within the polymeric[291] sheathing tube produced in step (a) by: (i) filling the interior space of the sheathing tube with a core solution ~~comprising a core~~[292] including at least one[293] polymerizable core[294] monomer,[295] which upon polymerization produces a polymeric core which[296] has a refractive index greater than that of the polymeric[297] sheathing tube; and (ii) allowing the core polymerizable monomer to polymerize~~ thereby forming a polymer having a refractive index greater than that of the sheathing tube such that the material is suitable to conduct light.~~[298] .[299] The core solution can ~~comprise an optional core dopant.~~[300] further include a core dopant.[301] When present, the core dopant

will have, for most embodiments, a refractive index greater than that of the polymer obtained upon polymerization of the core monomer (i.e. without addition of the dopant).[302]

~~a~~[303]

~~,~~[304]

~~will have a refractive index greater than that of the polymer obtained upon polymerization of the core monomer.~~[305]

~~The product thus obtained, is a graded index plastic optical material having an outer transparent sheathing~~[306]

In other aspects of the invention, the dopant included in the polymeric sheathing acts as a plasticizer, thus improving the mechanical properties of the polymeric sheathing. In other embodiments, a plastizer which does not provide a desireable dopant effect but which yields desirable mechanical properties may be used, or a dopant which does not act as a plasticizer may be used, or a combination of a dopant and a plasticizer may be used. In some preferred embodiments, the plasticizer added to the sheathing further can act as a dopant which raises or lowers the refractive index of the polymeric sheathing when compared to polymerized sheathing monomer not including the plasticizer. For embodiments involving conducting light within a rod or fiber fabricated according to the invention, preferrably the sheathing dopant lowers the refractive index of the polymeric sheathing.[307]

The terms "polymeric sheathing" and "polymeric core" as used herein refer to the polymerized sheathing and core solutions respectively, which include the polymerized sheathing and core monomers respectively (along with any agents involved with the polymerization reaction such as iniatiators, and chain transfer agents); plus, any added plasticizers and/or dopants, which do not participate in the polymerization reaction of the monomers. The terms "sheathing polymer" and "core polymer" as used herein, refer to the polymerized sheathing and core monomers respectively (along with any agents involved with the polymerization reaction such as iniatiators, and chain transfer agents), except polymerized without any plasticizers and/or dopants, which do not participate in the polymerization reaction of the monomers. "Sheathing polymer" and "core polymer" as used herein, may include homopolymers, copolymers, mixtures of homopolymers, mixtures of copolymers, mixtures of homopolymers and copolymers, and the like. A "dopant" as used herein, refers to any material or mixture of materials, which does not participate in the polymerization reaction and which is not covalently incorporated into the polymeric structure, but which has at least limited miscibility within the structure, so that when present, it alters the effective refractive index of the polymeric structure versus the refractive index of an equivalent polymer, but not containing the dopant, by at least 0.0001. A "plasticizer" as used herein, refers to any material or mixture of materials, which does not participate in the polymerization reaction and is not covalently incorporated into the polymeric structure, but which has at least limited miscibility within the structure, so that when present, it decreases the glass transition temperature of the polymeric structure versus that of an equivalent polymer, but not containing the plasticizer, by at least 1 %. It should also be understood that "plasticizers" and "dopants" as used herein also can include unreacted monomer, or unreacted agents typically used in conjunction with a polymerization reaction such as unreacted iniatiators, and unreacted chain transfer agents. Suitable dopants or plasticizers may be solids, liquids, or gases at room temperature and pressure.[308]

The phrase "transparent" or "at least partially transparent" as used herein, refers to the ability transmit or conduct a finite quantity of light energy (greater than zero) of at least one wavelength, over a finite, non-zero, distance. The term "coaxially" or "coaxial" as used herein to describe the structure of certain optical articles according to the invention, refers to an elongated cylindrical core having a central longitudinal axis, which is concentrically surrounded by, and in at least partial physical contact with, an outer annular sheathing, which shares the central longitudinal axis with the core, and is physically and/or chemically distinct from the core. The region of contact between the core and the sheathing is herein referred to as an "interface."[309]

Preferred products obtained by the methods of the invention include gradient index plastic optical articles having an outer transparent polymeric sheathing [310]layer and an inner transparent polymeric [311]core. The refractive index of the core is greater than that of the sheathing such that the ~~material~~[312]article[313] is suitable to conduct light, with the refractive index of the core ~~gradually decreasing in a radial direction from the center of the core~~[314]having a gradient in a specific direction. The term "refractive index" as used herein, refers specifically to the refractive index of the material at the wavelength, or wavelengths, of light being transmitted. When there may exist more than one index of refraction at a given wavelength within a material depending on the spatial location within the material where the index is measured, unless a specific spatial location is specified, the term "index of refraction" refers to the maximum index of refraction within the material. The phrase "gradient in a specific direction" as used herein, refers to a continuous change in a property in a radial direction either from the central axis[315] to the~~periphery. In general, the material is~~[316] periphery or vice versa. For preferred optical articles according to the invention, the core has a gradient in refractive index such that the refractive index is highest at the central axis of the core and decreases in the direction of the interface between the core and sheathing. However in other specific embodiments, the gradient may be in the opposite direction. In general, the articles are initially produced[317] in the shape of a preform rod, as shown in Figure 1, where the transparent sheathing is depicted as component 1 and the core is depicted as component 2. Preferably, the preform rod has a circular [318]cylindrical shape.~~ The method also provides~~[319] The methods of the present invention also provide[320] for forming a ~~graded~~[321]gradient[322] index plastic optical fiber~~. This comprises formation of a graded index plastic optical material, for example, as described above, in the shape of a preform rod followed by hot-drawing of the preform~~[323], preferrably with an outer diameter not more than 1 millimeter and with the same general cylindrical shape of the preform but with a smaller diameter. To form an optical fiber from a preform rod, the preform can be subjected to hot-drawing[324] at a temperature and speed suitable to render the fiber useful as an optical conductor. The novel addition of a plasticizer to the polymeric sheathing according to one aspect of the invention, provides improved mechanical properties of the preform article which enable faster hot-drawing speeds than previously attainable. For example, preforms, according to the invention, may be formed into an optical fiber able to conduct light at at least one wavelength with an attenuation less than 500 dB/km, and preferrably less than 200 dB/km, by hot drawing at a drawing speed of at least 3 m/min, preferrably at least 4 m/min, more preferrably at least 5 m/min, and even more preferrably at least 6

m/min. Alternatively, instead of formation of the optical fiber by hot drawing, the fiber may be produced by extrusion.[325]

The term "preform rod" as used herein ~~is the~~[326], refers to a[327] rod shaped ~~form of the graded~~[328] gradient[329] index plastic optical ~~material~~[330] article[331] that can subsequently [332] be ~~produced according to the method of the present~~[333] ~~invention. In general, the rod can be further~~[334] processed into an optical conductor such as an optical fiber, an optical waveguide,[335] or an optical integrated circuit. ~~For example, after the preform rod is produced, it can be removed from the polymerization container and formed into a~~[336] ~~plastic optical fiber. This can be accomplished, for example, by hot-drawing of the preform. Other known fiber producing techniques, for example, extrusion can also be employed.~~[337]

The polymerization container used in the method of the ~~35~~[338] invention can be composed of any material which is inert to

~~-8~~[339] the sheathing solution, for example, glass. The container shape and dimensions will determine the outer shape of the ~~graded~~[340] gradient[341] index plastic optical ~~material~~[342] preform article[343] ultimately obtained ~~in the practice of~~[344] by[345] the method. ~~A~~[346] The[347] sheathing tube ~~is~~[348] can be [349] produced~~,~~[350] by[351] using the well known technique of rotation casting, by placing a sheathing solution in the polymerization container and causing the solution to polymerize within the container ~~to give an inner~~[352] while the container is rotated to yield an annular[353] cylindrical ~~configuration.~~[354] shape. [355] Thus, the polymerization container can be any shape which when rotated about its own axis creates a sheathing tube with an ~~inner~~[356] annular[357] cylindrical ~~configuration.~~[358] shape. [359] The preferred shape of the container is ~~cylindrical,~~[360] a circular cylinder[361] preferably with dimensions ~~that can achieve a preform rod~~[362] suitable for hot-drawing into an optical fiber~~.~~[363]

~~The sheathing of the graded index optical material is the outer layer of the material. The sheathing is prepared using the well-known technique of rotation casting, by placing into a polymerization container a sheathing solution comprising a sheathing polymerizable monomer and a~~[364] ~~sheathing dopant and causing the sheathing polymerizable monomer of the sheathing solution to polymerize within the container in a cylindrical configuration. The sheathing dopant does not participate in the polymerization reaction. Polymerization of the monomer into a cylindrical~~[365] ~~configuration can be accomplished by, for example, rotating the polymerization container about its own axis, during polymerization.~~[366], for example, with an inner diameter between 0.25 and 2 inches. [367] The centrifugal force resulting from the rotation of the polymerization container [368] will cause the resulting polymer to form a tube of sheathing material or a sheathing tube within the polymerization container. Rotation can be accomplished, for example, by spinning the container.

~~Alternatively, the sheathing can also be prepared by extrusion of the doped sheathing polymer into tubular shapes using extrusion methods which are well known to~~[369]

~~those of skill in the art. The outer and inner shape of~~[370]

~~-9~~[371]

~~the sheathing in this method will be dictated by the shape of the extrusion dye. The extruded sheathing will then serve as the container into which the core solution will be added and allowed to polymerize.~~[372] The amount of sheathing-forming[373] solution placed in the polymerization container can be determined based upon the ratio of the thickness of the sheathing wall to the distance between the opposing interior walls of the sheathing~~,~~[374] which is desired. This ratio will depend upon the cost of materials and the end use of the optical ~~material~~[375] article[376].

Alternatively, the sheathing can also be prepared by extrusion of the sheathing polymer, together with any additives such as plasticizers and/or dopants, into tubular shapes using extrusion methods which are well known to[377] those of skill in the art. The outer and inner shape of the sheathing using this method will be dictated by the shape of the extrusion dye.[378] The extruded sheathing will then serve as the container into which the core-forming solution will be added and allowed to polymerize.[379]

The polymerizable sheathing monomer can be any monomer or mixture of monomers [380] which upon polymerization yields substantially amorphous and transparent polymeric materials. Preferably, the polymeric materials of the sheathing are at least partially soluble in the monomer present in the core-forming[381] solution and exhibit a suitable miscibility with the sheathing dopant and/or plasticizer[382].

Polymerizable monomers suitable for use in this invention include, but are not limited -[383] to, for example, methacrylate monomers such as branched and unbranched C~~1~~[384] 1-[385] C10 alkyl methacrylates, for example, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, n-hexyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate; halogenated methacrylates, such as 2,2,2-trifluoroethyl methacrylate; 4-methyl cyclohexyl methacrylate, cyclohexyl methacrylate, furfuryl methacrylate~~,~~[386] 1-phenylethyl methacrylate, 2-phenylethyl methacrylate, 1-[387] phenylcyclohexyl methacrylate, benzyl methacrylate and phenyl methacrylate; acrylate monomers such as, methyl acrylate, ethyl acrylate, n-butyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, methyl-a-chloro acrylate, 2,2,3,3-tetrafluoropropyl-a-fluoro acrylate , and 2,2,2-[388] trifluoroethyl acrylate; acrylonitrile and a-[389] methylacrylonitrile; vinyl monomers,[390] such as~~,~~[391] vinyl acetate,

~~10~~[392] vinyl benzoate, vinyl phenylacetate, vinyl chloroacetate; styrene monomers,[393] such as~~,~~[394] styrene, halogenated styrenes, for example, o-chlorosytrene, p-fluorostyrene, o,~~pdifluorostyrene~~[395] p-difluorostyrene[396], and p-isopropyl styrene; and[397] perfluorinated~~monomers such as 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3dioxole also known as~~[398] monomers such as those disclosed in European Patent Application EP 0710 855 herein incorporated by reference. Such monomers include, but are not limited to[399] perfluoro(2,2-dimethyl-1,3-dioxole) (PDD), perfluoro(allyl vinyl ether), perfluoro(butenylyl vinyl ether) [400] and any combination of monomers thereof. When a combination of monomers is employed polymerization will result in formation of a copolymer.

A sheathing plasticizer or[401] dopant suitable for use in the methods of the invention is one which does not participate in the chemical [402] reaction

which polymerizes the sheathing monomer. A ~~suitable~~[403] preferred[404] sheathing dopant will have a refractive index which is lower than that of the sheathing [405] polymer obtained upon polymerization of ~~the sheathing monomer of the sheathing solution.~~[406] sheathing monomer in a manner essentially identical to that employed for forming the polymeric sheathing except without the presence of the dopant. In other words, the sheathing dopant is selected so that the polymeric sheathing containing the sheathing dopant will have a lower refractive index than an equivalent polymeric sheathing except without the sheathing dopant by at least 0.0001, and preferrably by at least 0.0005. [407] In addition, the sheathing dopant ~~must not compromise the~~[408] should not unduly reduce the degree of[409] transparency of the ~~polymer~~[410] polymeric sheathing[411] obtained upon polymerization of the sheathing ~~monomer.~~[412] solution.[413] The level of transparency is inversely related to the transmission loss (i.e. attenuation) [414] of a ~~graded~~[415] gradient[416] index plastic optical conductor ~~in~~[417] at[418] the operating wavelength of the conductor, and can be assessed using techniques well [419] known to those of skill in the art. For example, a ~~graded~~[420] gradient[421] index plastic optical fiber which has a transmission ~~loss~~[422] lose[423] value of 110 dB/km at an operating wavelength of 650 nm, possesses an adequate level of transparency as an optical conductor. However, a loss of more than 500 dB/km would not be an acceptable level of transparency. Therefore, a ~~graded~~[424] gradient[425] index optical ~~material~~[426] article[427] is suitably[428] transparent when an optical conductor, prepared from the ~~material~~[429] article[430], has a transmission ~~loss~~[431] lose[432], also known as the attenuation, ~~in~~[433] for[434] the operating wavelength of the conductor less than 500 dB/km. Figure 2 depicts the transmission loss of an optical fiber prepared using the method of the invention as described herein in Example 1. The loss was measured using methods known in the art such as those described in "Test Method for Attenuation of All Plastic Multimode ~~Optical~~[435] optical[436] Fibers JIS C 6863-(1990)," Japanese Industrial Standard by the Japanese Standards Association~~.~~[437], herein incorporated by reference. [438] Figure 2 shows a transmission loss of 140 dB/km at a wavelength of 650 nm. ~~This transmission. loss provides a~~[439] ~~fiber with a suitable level of transparency.~~[440]

One useful criterion, for predicting whether or not the sheathing will be sufficiently [441] transparent, is predicated on the Flory-Huggins interaction parameter~~, XAB~~[442] ?AB[443]. That is, ~~XAB~~[444] ?AB[445] can be used as a guide to the ~~likelihood~~[446] degree[447] of miscibility between substances A and B, which in this case would be sheathing polymer and sheathing plasticizer and/or [448] dopant. The blend miscibility can be assumed to decrease with increasing values of ?AB. This parameter can be determined experimentally or approximated according to the following equation:

~~6,~~[449] where d[450] is the solubility parameter which is a thermodynamic quantity generally defined as the square root of the cohesive energy density~~. The~~[451] (the[452] cohesive energy density is obtained by dividing the molar evaporation energy, ~~DE~~[453] ?E[454], of a liquid by a molar volume, V~~.~~[455]),[456] Vref is an appropriate reference volume~~. —~~[457], [458] R is the ideal [459] gas constant and T is the temperature~~.~~[460] in degrees K. [461] A detailed discussion of the Flory-Huggins interaction parameter can be found in CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility-[462] Parameters, by A.F.M. Barton, ~~1990.~~[463] 1990, herein incorporated by reference. Flory-Huggins interaction parameters below

about 0.5 generally indicate that a dopant or plasticizer may have suitable miscibility for use in the invention. [464]However, the Flory-Huggins interaction parameter should be used only [465]as a guide to the selection of an appropriate dopant or plasticizer[466], but not as a limitation, since the concentration of the plasticizer or [467]dopant is also ~~an~~[468] important ~~criterion to consider in maintaining a~~[469]in determining the transparency of the polymeric[470] sheathing and core ~~with an acceptable transparency~~[471].

Some examples of preferred [472]sheathing dopants suitable for use in the invention include, but are not limited to, diisobutyl

~~-12~~[473] adipate, glycerol-triacetate, 2,2,4-trimethyl- 1,3-[474]pentanediol diisobutyrate, methyl laurate, dimethyl sebatate, isopropyl myristate, diethyl succinate, diethyl phthalate, tributyl phosphate, dicyclohexyl phthalate, dibutyl sebatate, diisooctyl phthalate, dicapryl phthalate, diisodecyl phthalate, butyl, octyl phthalate, dicapryl adipate, perfluorinated aromatics, for example perfluoro naphthalene, perfluorinated ethers and perfluorinated polyethers. ~~Typically~~[475]Preferably[476], the sheathing dopant is present in the sheathing at ~~a~~[477]an overall[478] concentration of between about 1 and about 35 weight percent based on the total weight [479]of the ~~monomer of the~~[480]polymeric[481] sheathing ~~solution~~[482], more ~~typically~~[483]preferably[484] between about 1 and about 20 weight percent,[485] and most ~~typically~~[486]preferably[487] between about 1 and about 15 weight percent. In general, ~~the~~[488]preferred[489] sheathing ~~dopant~~[490]dopants[491] can also[492] impart plasticizer-like qualities and/or hydrophobic properties ~~upon the graded index plastic optical material.~~[493]to the polymeric sheathing. [494] The presence of plasticizer-like qualities and/or hydrophobic properties in the ~~graded index plastic optical material of~~[495]polymeric sheathing of [496]the invention is advantageous. That is, plasticizer-like qualities allow the ~~graded~~[497]gradient[498] index plastic optical ~~material~~[499]article[500] to be hot-drawn at a lower temperature and a higher speed, ~~which results~~[501]and also can result[502] in a fiber with ~~an acceptable~~[503]a lower[504] level of attenuation or transmission loss compared to prior art fibers and methods[505]. Hydrophobic properties provide for an optical ~~material~~[506]article[507] with enhanced environmental stability, for example~~,~~[508] decreased moisture absorbency.

~~Any method of polymerization can be used in the method of the invention for forming the graded~~[509]It should be emphasized that, in some embodiments, a plasticizer can be used to impart the desirable physical properties above that does not impart desired refractive index changes to the polymer. Such a plasticizer may advantageously be used alone when changes in refractive index are not needed or desired, or, in other embodiments, such plasticizers may be used together with a separate dopant. Any suitable plasticizer known in the art useful for plasticizing the polymers formed from the polymerizable monomers previously listed may potentially be employed in the present invention. [510]

Suitable methods of polymerization for forming the gradient[511] index plastic optical ~~material. These methods~~[512]article according to the invention[513] include, for example, free radical polymerization, atom transfer radical polymerization, anionic polymerization and cationic polymerization. Free radical bulk polymerization, employing either thermal or optical energy, is preferred.

When radical polymerization is employed, the sheathing solution also includes a radical polymerization initiator

~~-13~~[514] and a chain transfer agent~~.~~[515] which participate in the polymerization reaction. [516] Suitable radical polymerization initiators are selected based on the type of energy employed in the polymerization reaction. For example, when heat or infrared ~~polymerization~~[517] energy[518] is employed, [519] peroxides such as lauryl peroxide, benzoyl peroxide, ~~tbutyl~~[520] t-butyl[521] peroxide and 2,5-dimethyl-2,5-di(2-ethyl hexanoyl peroxy)hexane (TBEC) are suitable for use. When ultraviolet ~~polymerization~~[522] light energy[523] is employed benzoin methyl ether (BME) or benzoyl peroxide is suitable for use. Typically, the polymerization initiator is present in the sheathing solution in a range of between about 0.1 to about 0.5 percent by weight ~~of the monomer~~[524].

~~Any chain~~[525] Chain[526] transfer ~~agent is~~[527] agents[528] suitable for use in the method of the invention~~. These~~[529] include, but are not limited to, 1-butanethiol and 1-dodecanethiol. Typically, the chain transfer agent ~~is~~[530] in[531] present in the sheathing solution below about 0.5 percent by weight ~~of the monomer~~[532].

As described earlier, the polymerization container is rotated during polymerization of the monomer of the sheathing solution. This rotation, for example~~,~~[533] spinning, ~~provides~~[534] will yield[535] a transparent sheathing tube having an ~~inner~~[536] annular[537] cylindrical configuration. The interior space of this sheathing tube thereby provides a suitable container for polymerization of the core monomer in a subsequent step of the ~~claimed~~[538] inventive[539] method.

The core of the ~~graded~~[540] gradient[541] index plastic optical ~~material~~[542] article[543] is the inner layer of the material which is disposed within the sheathing. The core is transparent and ~~ultimately provides~~[544] is[545] the component of the ~~material~~[546] article[547] through which most of the [548] light travels. The refractive index of the central axis of the polymeric [549] core is preferably [550] greater than that ~~of the sheathing such the material is suitable to conduct light.~~[551] of the sheathing, and more preferably, the index of refraction throughout the bulk of the core is greater than that of the polymeric sheathing. [552]

The core can be prepared by filling the sheathing tube with a core solution ([553] which ~~comprises a core polymerizable 35 monomer and an optional~~[554] includes a polymerizable core monomer and, optionally, a[555] core dopant)[556], and polymerizing the

~~-14~~[557] ~~core monomer.~~[558] core monomer in the solution. [559] The ~~core polymerizable~~[560] polymerizable core[561] monomer can be any monomer or mixture of monomers[562] which upon polymerization yields substantially amorphous and transparent polymeric materials capable of conducting light ~~in~~[563] at[564] the desired wavelength. In addition, the ~~core polymerizable monomer, upon polymerization,~~[565] polymeric core, once formed, preferably[566] has a refractive index at its central axis [567] greater than that of the sheathing such that the ~~material~~[568] final optical article[569] is suitable to conduct light. All of the monomers which are suitable for use in preparing the sheathing are, likewise, suitable for use in preparing the ~~core. A combination of monomers can also be~~

~~used in preparation of the core thereby providing a core comprising a copolymer.~~[570] core.[571]

~~As described earlier, any~~[572]Any[573] method of polymerization ~~is suitable for use in the method of the invention. When~~[574]previously described as suitable for formation of the polymeric sheathing is also suitable for formation of the polymeric core. When [575]radical polymerization is employed in preparation of the core~~,~~[576] a polymerization initiator and chain transfer agent [577]is present in the core solution ~~in ranges~~[578]with a concentration[579] similar to ~~those~~[580]that[581] described earlier for the sheathing~~ solution. Typically, the chain transfer agent is present below about 0.5 percent by weight of the~~[582] .[583] ~~monomer.~~[584]

~~A~~[585]An optional[586] core dopant suitable for use~~ in the method of the invention~~[587] is one which does not participate in the chemical [588]reaction which polymerizes the core monomer and which preferably [589]has a boiling point lower than the highest processing temperature to which it is subjected. A suitable core dopant will preferably [590]have a refractive index which is greater than that of the core [591]polymer obtained upon polymerization~~ of the~~[592] of a[593] core monomer solution without the core dopant[594]. In addition, ~~the~~[595]preferred[596] core ~~dopant must~~[597]dopants should[598] not ~~compromise~~[599]unduly reduce[600] the transparency of the ~~polymer obtained upon polymerization of~~[601] ~~the~~[602]polymeric[603] core~~ monomer~~[604]. As in the preparation of the sheathing, one useful criterion for predicting whether or not the core will be sufficiently [605]transparent is predicated on the Flory-Huggins interaction parameter~~,~~[606] between the core polymer and the core dopant. However, as discussed earlier this parameter should be used only as a guide ~~not a limitation~~ [607]when

~~-15~~[608] choosing a suitable core dopant, since the concentration of the dopant also ~~needs to be considered~~[609]affects the polymeric core transparency[610].

Compounds suitable for use as the core dopant in the method of the invention include, but are not limited to, dibenzyl ether, phenoxy toluene, 1,1-bis-(3,4-dimethyl phenyl) ethane, diphenyl ether, biphenyl, diphenyl sulfide, diphenylmethane, benzyl phthalate-n-butyl, 1-methoxyphenyl-[611]1-phenylethane, benzyl benzoate, bromobenzene, ~~odichlorobenzene~~[612]o-dichlorobenzene[613], m-dichlorobenzene, 1,2-dibromomethane, 3-[614]phenyl-~~1~~[615],[616] 1-propanol, dioctyl phthalate and perfluorinated aromatics, such as, perfluoro naphthalene.

When the core solution, which ~~comprises~~[617]includes[618] the core monomer and an optional core dopant, is added to the sheathing tube, the inner surface of the sheathing tube~~,~~[619] is slightly swollen by the core monomer.~~ As a result~~[620] During the polymerization[621], a gel phase is formed ~~on~~[622]in the polymerizing core adjacent to[623] the inner wall of the sheathing tube~~. The concentration of the polymer in the swollen-phase layer is not uniform, in that the concentration of the polymer and sheathing dopant, eluted from the sheathing, gradually~~[624] which gradually moves toward the central axis as the polymerization process progresses. Since the diffusivity of the core dopant is higher in the unpolymerized core solution than in the gel phase or the polymerized regions of the core, there is a net migration of core dopant towards the central axis of the core during the polymerization, so that when polymerization is complete,

there is a concentration gradient of core dopant in the direction from the central axis (highest concentration) towards the interface with the sheathing (lowest concentration). In contrast, the sheathing dopant, some of which can elute from the sheathing and diffuse into the core during polymerization, will have a concentration within the polymerized core which is highest at the core-sheathing interface and which gradually [625]decreases with distance from the ~~inner surface.~~[626]interface towards the central axis of the core. [627] Thus, a ~~distributed~~ [628]concentration gradient[629] of the low refractive index sheathing [630]dopant is formed in the gel phase during polymerization[631] due to diffusion of sheathing dopant~~. Polymerization~~[632] from the polymeric sheathing. The polymerization front in the core[633] starts from the vicinity of the inner surface of the sheathing (interface between sheathing and core) [634]and gradually ~~grows~~[635]~~to~~[636]moves towards[637] the center axis of the ~~tube~~[638]core[639] due ~~to~~[640]a phenomena of[641] accelerated polymerization in the gel ~~stated~~[642]phase[643] commonly known as the "gel-effect" (~~See~~[644]For additional details, see[645] for example, Koike, Y. et al., "~~HighBandwidth~~[646]High-Bandwidth[647] Graded-Index Polymer Optical Fiber~~,~~[648]",[649] Journal of Lightwave Technology, ~~13(7~~[650]230[651]): 1475-1489 (1995) and Koike, Y. et al., "New Interfacial-Gel Copolymerization Technique for Steric GRIN Polymer Optical Waveguide and Lens Arrays~~,~~[652]",[653] Applied ~~optics~~[654]Optics[655], 27(3): 486-491 (1988), both incorporated herein by reference[656]).

~~When~~[657]As discussed above, when[658] a core dopant, having a higher refractive index than the equivalent polymerized core monomer but without the core dopant,[659] is present, a concentration gradient of the core dopant, ~~which remains in~~[660]within[661] the polymeric [662]core~~polymer~~[663], is~~ also~~[664] formed. As described in U.S. Patent No.

~~L)~~[665]

~~-16~~[666] 5,541,247 by Koike, incorporated herein by reference, [667]the core monomer polymerizes while the substance with a greater refractive index (core dopant) [668]becomes ~~highly~~ [669]concentrated ~~at~~[670]towards[671] the ~~center~~[672]central axis[673] of the core. The high concentration of the core dopant which is present at the central part of the core gradually decreases in a radial direction toward the periphery, thereby, creating a gradient in ~~a specific direction.~~[674]core dopant concentration in a specific direction which creates a corresponding gradient in refractive index within the core. Notably, the specific direction of the concentration gradient of core dopant within the polymeric core will be opposite that of the concentration gradient of the sheathing dopant within the core.[675]

~~In a certain embodiment, the~~[676] In certain embodiments, the polymerizable[677] monomer of the sheathing solution and the polymerizable [678]monomer of the core solution are the same.~~Suitable~~[679] In such cases, suitable[680] monomers include those which form polymers that are substantially amorphous and transparent, thereby being capable of conducting light ~~in~~[681]at[682] the desired wavelength, as earlier described.~~ when~~[683] When[684] the sheathing and core monomers are the same, and a core dopant is present, the sheathing dopants [685]and core dopants will be different. That is, the sheathing dopant will have a refractive index which is less than that of the polymer obtained upon an equivalent [686]polymerization of ~~the~~[687]a[688] sheathing monomer solution without the sheathing dopant,[689] while the core dopant will have a refractive index which is greater

than that of the polymer obtained upon an equivalent [690] polymerization of ~~the~~[691] a[692] core monomer~~. However~~[693] solution without the core dopant. Preferably[694], the difference in refractive index between the sheathing dopant and core dopant should have a value which renders the optical ~~material~~[695] article[696] suitable to conduct light at at least one wavelength with an attenuation less than 500 dB/km[697].

~~This difference in the refractive index could be, for~~[698]

Advantageously, through use of a low refractive index sheathing dopant according to one aspect of the invention, the overall concentration of core dopant required to provide a desired difference in refractive index between the central axis of the core and the sheathing will be less than for an equivalent optical article except having a sheathing which does not include the sheathing dopant. The term "overall concentration" as used herein, refers to the total amount of core dopant present in the polymeric core based on the total weight of the polymeric core. In short, the current invention provides plastic optical articles which require a lower overall concentration of core dopant to obtain comparable bandwidth capabilities when compared to similar prior art optical articles. The ability to use a lower overall core dopant concentration provides many advantages in the optical and physical properties of the articles as discussed below. As an example, if a desired difference in the refractive index between the central axis of the core and the sheathing is 0.001, this could be achieved according to the present invention, for example, by employing a core dopant which raises the refractive index the polymeric core by 0.0005 and a sheathing dopant which lowers the refractive index of the polymeric sheathing by 0.0005. The use of a low refractive index sheathing dopant according to the invention enables the fabrication of plastic optical articles having an unprecedented difference in the refractive indices of the central axis of the core and the sheathing. For example, according to the inventive methods, using a particular selection of dopants, a plastic optical preform can be fabricated with the difference in the refractive indices between the central axis of the core and the sheathing being at least 0.01 with an overall core dopant concentration not exceeding 12 %wt.[699]

~~example, 0.001 and be achieved by, for example, employing a core dopant with a refractive index greater than that of the core polymer by 0.0005 and a sheathing dopant with a refractive index less than of the sheathing polymer by 0.0005.~~[700] Thus, the method of the invention employing sheathing dopants [701] has advantages over a method employing a dopant-free sheathing, in that for example,[702] a broader selection of materials which can employed as dopants is available, based on the additive effect of the core and sheathing dopant as opposed to the singular effect of ~~the~~[703] a[704] core dopant alone[705]. Additionally, a lower concentration of

~~-17~~[706] core [707] dopant or no dopant at all can be used in the core ~~and still achieve a comparable difference in refractive index.~~[708] while still achieving a suitable difference in refractive indices. A reduction in the required concentration of core dopant can, for example, increase the transparency of the article and reduce attenuation when compared to an equivalent article except having a sheathing without the sheathing dopant, such article thus requiring a higher overall concentration of core dopant to create the same difference in refractive index between the central axis of the core and the sheathing. "Equivalent" as used herein in this context implies that all materials and polymerization conditions are the same for the articles being compared except

for the presence of a dopant or plasticizer. The reduction in core dopant concentration enabled by the present invention can also allow for an increased maximum service temperature for the article, since lower core dopant concentrations will typically correlate with higher glass transition temperatures for the polymeric cores. For example, the present invention can provide a plastic optical article comprising a polymeric sheathing and a polymeric core where the refractive index at the central axis of the core exceeds that of the sheathing (for the same wavelength) by at least 0.01, while the article has a maximum service temperature of at least 40 degrees C.[709]

In a specific ~~embodiment, the monomer of~~[710]preferred embodiment, the monomer that is polymerized to form[711] the core and the sheathing is methyl methacrylate. In ~~this embodiment,~~[712] ~~when a core dopant is present, the sheathing and core dopants are different substances. The difference in the refractive index between the dopants must be such that the optical material is suitable to conduct light. Additionally, the refractive index of the core dopant is~~[713] ~~greater than that of the sheathing dopant. For example, the dopant for the sheathing can be tributyl phosphate (refractive index = 1.424) while the dopant for the core can be diphenyl sulfide (refractive index = 1.6327).~~[714] ~~In another embodiment, the monomer of the core and the~~[715]~~sheathing is 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3dioxole also known~~[716]another preferred embodiment, the monomer that is polymerized to form the core and the sheathing is a perfluorinated monomer such[717] as perfluoro(2,2-dimethyl-~~1,3~~[718]1,3[719]-dioxole) (PDD). In ~~this embodiment~~[720]these embodiments[721], when a core dopant is present, the sheathing ~~and core dopants are~~[722]plasticizer and/or dopant and core dopant are preferably[723] different substances~~, with~~[724]. For embodiments where the sheathing includes a sheathing dopant,[725] the difference in the refractive index between the~~dopants~~[726] dopants should be[727] such that the optical ~~material~~[728]article[729] is suitable to conduct light~~. Additionally, the refractive index of the core dopant is greater than that of the sheathing dopant.~~[730]

~~In yet another embodiment, the method of the invention further comprises the step of hot-drawing the graded index~~[731] ~~optical preform into a fiber. Typically, hot-drawing is conducted at a temperature suitable to sufficiently soften the preform rod to allow it to be drawn into a fiber. The drawing is generally conducted at a speed suitable to render the fiber useful as an optical conductor.~~[732]

~~In yet another aspect, the invention provides a graded index plastic optical material comprising: (a) a transparent sheathing comprising a sheathing polymer and a sheathing dopant, wherein the sheathing dopant has a refractive index which is less than that of the sheathing~~[733] ~~polymer; and (b) a transparent core, disposed within the~~[734]

~~-18~~[735]

~~sheathing, comprising a core polymer having a refractive index greater than that of the sheathing and an optional core dopant, the core dopant, when present, having a refractive index which is greater than that of the core~~[736] ~~polymer; wherein the core dopant has a concentration gradient in a specific direction. The refractive index of the core is greater than the doped sheathing.~~[737]

~~In a preferred embodiment, the graded index plastic optical material is in the shape of a cylindrical preform~~[738]

~~rod. In another application, the graded index plastic optical material is in the shape of a cylindrical fiber having an outer diameter between about 0.2 millimeters and about 1 millimeter. The fiber can be prepared, for example, by hot-drawing a preform rod, the fiber~~[739] ~~maintaining the same geometry of the preform but, with a smaller outer diameter.~~[740]

~~In certain embodiments, the graded index plastic optical material has the same polymer in both the sheathing and the core. In this particular embodiment, when the~~[741] ~~optional core dopant is present, the core dopant and the sheathing dopant are different substances. The sheathing dopant has a refractive index which is less than that of the core dopant. The difference in refractive index between the dopants should be such that resulting optical~~[742]~~material is suitable to conduct light. For example, the material should be useful as an optical conductor. For example, when the polymer of the core and sheathing is~~[743] at the desired wavelength. Additionally, for such embodiments, the refractive index of the core dopant is preferably greater than that of the sheathing dopant. For example, when the core polymer and sheathing polymer are[744] poly(methyl methacrylate), the dopant for the [745]sheathing ~~dopant can~~[746]could[747] be tributyl phosphate (refractive index = 1.424) ~~and~~[748]while[749] the ~~core~~[750]~~dopant can~~[751]dopant for the core could[752] be diphenyl sulfide (refractive index = 1.6327). ~~When the polymer of the core and sheathing is, for example, that obtained upon polymerization of the monomer 2,2bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, the sheathing dopant and core dopant are different substances,~~[753] ~~with the difference in the refractive index between the~~[754]

~~-19~~[755]~~dopants such that the optical material is suitable to conduct light. In addition, the refractive index of the core dopant is higher than the sheathing dopant with both dopants being~~[756]Other preferred embodiments where the sheathing and the core include the same polymerized monomer, for example a perfluorinated monomer, utilize different sheathing and core dopants where both dopants are[757] perhalogenated.

~~The advantages~~[758] A significant advantage[759] of the ~~method~~[760]methods[761] of the invention include the availability of a significantly broader range of dopant and monomer [762]materials which are useful in preparing ~~a graded~~[763]the inventive gradient[764] index plastic optical ~~material.~~[765]articles. [766] This increase in the range and[767] types of materials suitable for use in the invention provides, for example, the ability to increase the difference in the refractive ~~index~~[768]indices[769] between the sheathing and the core without unduly[770] compromising the performance [771]characteristics of the optical ~~material~~[772]article,[773] and, in some cases,[774] the ability to widen the operating wavelength range [775]of the ~~material~~[776]articles. This is[777] particularly important [778]when the articles are[779] employed in data communications~~.~~[780] applications. [781]In addition, the concentration of dopant in the core, necessary to provide the required difference in refractive ~~index~~[782]indices[783], can be decreased when a sheathing dopant, ~~having a lower~~[784]which lowers the[785] refractive index ~~than~~[786]of[787] the polymeric[788] sheathing~~-polymer~~[789], is present. This decrease in the required [790]concentration of the core dopant can[791] significantly ~~improves~~[792]improve[793] the miscibility of the core dopant [794]materials which directly impacts the optical

characteristics, for example, transparency of the optical ~~material. Further~~[795] article. Furthermore[796], the sheathing dopant, in many instances, ~~behaves as a plasticizer in the graded index plastic optical material.~~[797] will also behave as a plasticizer. Plasticizers, including plasticizing dopants, can enable hot-drawing of the preform article according to the invention into, for example, an optical fiber at a lower temperature and/or higher drawing speed as previously discussed.[798]
~~This plasticizer-like behavior allows for hot-drawing of the material, for example, in the shape of a preform rod at a lower temperature and/or higher speed.~~[799]

Plasticizers, including plasticizing dopants, also provides advantages when forming the optical preform article during polymerization. In typical prior art methods not employing a sheathing plasticizer, when the core monomer is polymerized within the sheathing tube, the core has a tendency to shrink in a radial direction as polymerization proceeds. This results in the polymeric core separating from the sheathing during the polymerization causing the formation of bubbles at the interface between the sheathing and the core for a significant fraction of the articles produced. These bubbles are very detrimental to the optical performance of the article, and normally are cut out of the article, thus reducing its length, or the article containing the bubbles is simply discarded. With the present invention, the sheathing plasticizer can soften the polymeric sheathing, by lowering the glass transition temperature, an effective amount so that the sheathing will remain in contact with the core to a greater extent during core polymerization. In this way, the quantity of bubbles formed at the interface can be markedly reduced. Specifically, the present invention provides a method for the consistent production of plastic optical articles, each having an interface between the polymeric sheathing and polymeric core that is essentially free of visible bubbles. The mechanical property advantages of including dopants and/or plasticizers in the sheathing are not limited to applications involving gradient index plastic optical articles. Similar advantages, for example an increase in permissable drawing speed, may be realized for step-index plastic optical articles, plastic optical lenses, plastic optical waveguides, and plastic optical integrated circuits.[800]

The invention will now be further illustrated by the following examples which are not intended to limit the scope of the invention in any way. All percentages are by weight unless otherwise specified.

~~-20~~[801]

~~EXEMPLIFICATION~~[802]
EXAMPLE 1:

PREPARATION OF SHEATHING

A sheathing solution containing 1600 g (92.2 %wt) [803] of purified methyl methacrylate (MMA), 4.00 g (~~0.25 weight percent of MMA~~[804] 0.23 %wt[805]) of lauryl peroxide as the polymerization initiator, 3.42 ml of 1-butanethiol (~~0.18 weight percent of MMA~~[806] 0.17 %wt[807]) as the chain transfer reagent (available from Aldrich Chemical Co., Inc.~~,~~[808] .[809] Milwaukee, WI) and 128 g ~~(8 weight percent of~~[810] ~~MMA)~~ [811] of dicyclohexyl phthalate (7.4 %wt) as the sheathing dopant [812] was stirred and degassed for about 30 minutes.

To an appropriately stoppered glass tube, having an inner diameter of 30 mm and a length of 1.5 meters was added sheathing solution, to ~~the appropriate~~[813] a[814] height of 1 meter [815] to achieve ~~the desired~~[816] a[817] final ratio of

core to sheathing thickness~~. For example~~[818] of about 2:3. In general[819], a final ratio of the thickness of the sheathing wall to core thickness can be between about 1:4 to about 2:1. Both ends of the tube were sealed, and then the tube was placed in a water bath at a temperature of 71~~°~~[820] degrees [821]C and polymerized while being rotated at approximately 500 rpm for 20 hours. The tube was then placed in a rotating oven (approximately 5 rpms) for two hours at 100~~°C. A poly(methyl methacrylate)~~[822] degrees C. A polymeric[823] sheathing tube was ~~prepared~~[824]thus obtained[825].

PREPARATION OF CORE~~:~~[826]

The sheathing prepared above was kept in the glass tube, and the container formed by the cylindrical inner surface of the sheathing was filled with a solution containing 350 g (92.1 %wt) [827]of MMA, 200 microliters of t-butyl peroxide, 600 microliters of 1-dodecanethiol and 30 grams ~~(8.5 weight percent~~[828] (7.9 %wt[829]) of diphenyl sulfide~~.~~[830] as the core dopant. [831] The tube was sealed and then heated in a vertical position at 90~~°~~[832] degrees [833]C for ~~at least 12~~[834]24[835] hours. The tube was then placed in the oven horizontally and heated for 12 hours at 90~~°~~[836] degrees [837]C, 24 hours at

~~-21~~[838]~~110°~~[839] 110 degrees [840]C, 10 hours at 120~~°~~[841] degrees [842]C and 4 hours at 130~~°~~[843] degrees [844]C while rotating at a speed of 5 ~~rpms~~[845]rpm[846].

The ~~graded~~[847]gradient[848] index plastic optical preform rod was then removed from the glass polymerization container. The rod was then slowly inserted into a cylindrical heating furnace from the top while the furnace was maintained at a temperature between 180~~°~~[849] degrees [850]C and 220~~°~~[851] degrees [852]C. When the rod was softened sufficiently, hot-drawing and [853]spinning into an optical fiber [854]at a constant speed of approximately ~~5-~~[855]15 ~~meters~~[856]m[857]/min was started from the bottom of the rod.

EXAMPLE 2~~:~~[858]

PREPARATION OF SHEATHING

A polymeric sheathing was prepared as in Example 1 above, except that the [859]sheathing solution ~~containing 1600 g of purified methyl methacrylate (MMA), 4.00 g (0.25 weight percent of~~[860]~~MMA) of lauryl peroxide as the polymerization initiator, 3.42 ml of 1-butanethiol (0.18 weight percent of MMA) as the chain transfer reagent (available from Aldrich Chemical Co., Inc., Milwaukee, WI) and 320 g (20 weight percent of MMA~~[861]contained 320 g (16.6 %wt[862]) of dicyclohexyl phthalate ~~was stirred and degassed for~~[863]as the sheathing dopant. [864] ~~about 30 minutes.~~[865]

~~To an appropriately stoppered glass tube, having an inner diameter of 30 mm and a length of 1.5 meters was added sheathing solution, to the appropriate height to achieve the desired final ratio of core to sheathing~~[866] ~~thickness. For example, a final ratio of sheathing to core thickness can be between about 1:4 to 2:1. Both ends of the tube were sealed, and then the tube was placed in a water bath at a temperature of 71°C and polymerized while being rotated at approximately 500 rpm for 20 hours. The~~[867] ~~tube was then placed in a rotating oven (approximately 5 rpms) for two hours at 100°C. A poly(methyl methacrylate) sheathing tube was prepared.~~[868]

~~22~~[869]

PREPARATION OF CORE:

~~The sheathing prepared above was kept in the glass tube, and the container formed by the inner surface of the sheathing was filled with a solution containing 350 g of~~[870] A polymeric core, preform rod and optical fiber were prepared as in Example 1 above, except that the core solution contained no added core dopant.[871]

~~MMA, 200 microliters of t-butyl peroxide and 600 microliters of 1-dodecanethiol. The tube was sealed and then heated in a vertical position at 90°C for at least 12 hours. The tube was then placed in the oven horizontally and heated for 12 hours at 90°C, 24 hours at 110°C, 10~~[872]

~~hours at 120°C and 4 hours at 130°C while rotating at a speed of 5 rpms.~~[873]

~~The graded index plastic optical preform rod was then removed from the glass polymerization container. The rod was then slowly inserted into a cylindrical heating furnace~~[874]

~~from the top thereof while the furnace was maintained at a temperature between 180°C and 220°C. When the rod was softened sufficiently, spinning at a constant speed of approximately 5-15 meters/min was started from the bottom~~[875]

~~of the rod.~~[876]

EXAMPLE 3[877]

A polymeric sheathing, polymeric core, plastic optical preform rod, and optical fiber were prepared as outlined in Example 1, except that 2,2,4-trimethyl-1,3-pentanediol diisobutyrate was substituted for dicyclohexyl phthalate as the sheathing dopant.[878]

EXAMPLE 4[879]

A polymeric sheathing, polymeric core, plastic optical preform rod, and optical fiber were prepared as outlined in Example 2, except that 2,2,4-trimethyl-1,3-pentanediol diisobutyrate was substituted for dicyclohexyl phthalate as the sheathing dopant.[880]

EXAMPLE 5[881]

A polymeric sheathing, polymeric core, plastic optical preform rod, and optical fiber were prepared as outlined in Example 1, except that diethyl succinate was substituted for dicyclohexyl phthalate as the sheathing dopant.[882]

EXAMPLE 6[883]

A polymeric sheathing, polymeric core, plastic optical preform rod, and optical fiber were prepared as outlined in Example 2, except that diethyl succinate was substituted for dicyclohexyl phthalate as the sheathing dopant.[884]

~~EQUIVALENTS~~[885]

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

~~23~~[886]

~~CLAIMS~~[887]

~~What is claimed is:~~[888]
Claims[889]

1. A ~~graded~~[890] gradient[891] index plastic optical ~~material~~[892] article[893] comprising: ~~a) a~~[894] a polymeric sheathing, which is at least partially[895] transparent to light at at least one wavelength, including a [896] sheathing ~~having a sheathing~~[897] polymer and a sheathing dopant, the sheathing dopant having a refractive index which is less than that of the ~~sheathing polymer; and~~[898] an equivalent polymeric sheathing without the sheathing dopant; and[899] ~~b) a transparent core disposed within the sheathing, comprising a core polymer having a refractive~~[900] ~~index greater than that of the sheathing and an optional core dopant~~[901] a polymeric core, including a core polymer, coaxially disposed within said sheathing, said core being at least partially transparent to light at at least one wavelength and[902] having a gradient in[903] refractive index ~~which is greater than that of the core polymer; wherein the core dopant has a concentration gradient~~[904] in a specific direction.

2. The ~~material~~[905] article[906] of ~~Claim 1~~[907] claim 1,[908] wherein said sheathing dopant lowers [909] the refractive index of the ~~transparent core is greater than that of the transparent sheathing such that the material is~~[910] ~~suitable to conduct light~~[911] polymeric sheathing by at least 0.0005 compared to an equivalent sheathing without said sheathing dopant[912].

~~3. The material of Claim 1 in the shape of a cylindrical preform rod.~~[913]
3. The article of claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 35 %wt.[914]

~~4. The material of Claim 1 in the shape of a cylindrical fiber having an outer diameter between about 0.2 millimeters and about 1 millimeter.~~[915]
4. The article of claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 20 %wt.[916]

5. The ~~material~~[917] article[918] of ~~Claim 1 wherein the sheathing and core polymers are formed from different polymerizable monomers~~[919] claim 1, wherein said sheathing dopant is present in the polymeric sheathing at an overall concentration less than 15 %wt[920].

6. The ~~material~~[921] article[922] of ~~Claim 1 wherein the sheathing and core polymers are formed from the same polymerizable 30 monomer~~[923] claim 1, wherein the interface between said polymeric sheathing and said polymeric core is essentially free of visible bubbles[924].

~~-24~~[925]
~~7. The material of Claim 6 wherein the polymerizable monomer is methyl methacrylate.~~[926]

7. The article according to claim 1, wherein said polymeric sheathing and said polymeric core are both at least partially transparent to the same at least one wavelength of light.[927]

8. The ~~material~~[928] article[929] of ~~Claim 7 wherein the sheathing dopant is dimethyl sebatate~~[930] claim 1, wherein said polymeric core further includes a core dopant having a refractive index which is greater than that of an equivalent polymeric core without the core dopant[931].

9. The ~~material of Claim 8 wherein the core dopant is benzyl benzoate.~~[932] article according to claim 8, wherein the refractive index of the central axis of the polymeric core exceeds that of the polymeric sheathing by at least 0.01.[933]

10. ~~The material of Claim 7~~[934] The article according to claim 9,[935] wherein the ~~sheathing dopant is diisobutyl adipate~~[936] overall concentration of said core dopant in said polymeric core is less than 12 %wt[937].

~~11. The material of Claim 10 wherein the core dopant is benzyl benzoate.~~[938] 11. The article of claim 9, wherein said article has a maximum service temperature of at least 40 degrees C.[939]

~~12. The material of Claim 6 wherein the polymerizable monomer is 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3dioxole.~~[940]

~~13. The material of Claim 1 wherein the core dopant is not present.~~[941]
12. The article of claim 8, wherein said core dopant has a concentration gradient within said core in the same direction as the gradient in refractive index.[942]

~~14. A method for forming a graded index plastic optical~~[943]
~~material, comprising the steps of:~~[944]
~~(a) providing a transparent tube of sheathing~~[945]
~~material comprising a sheathing polymer and a sheathing dopant; and~~[946]
~~(b) forming a transparent core, within the sheathing tube produced in step (a), said core having a refractive index greater than that of the sheathing tube by:~~[947]
13. The article of claim 12 wherein, said polymeric core further includes said sheathing dopant having a concentration gradient within the core in a specific direction opposite that of said direction of the concentration gradient of the core dopant.[948]

~~-25~~[949]
~~(i) filling the sheathing tube with a core solution comprising a core polymerizable monomer, which upon polymerization, has a refractive index greater than that of the~~[950]
~~sheathing tube and with an optional core dopant having a refractive index greater than that of the polymer obtained upon polymerization of the core monomer; and~~[951]
~~(ii) polymerizing the core monomer of the core~~[952]

~~solution to form a graded index plastic optical material having an outer sheathing and an inner core.~~[953]

14. The article of claim 1, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.[954]

15. ~~The method of Claim 14 wherein the sheathing tube is made by:~~[955] The article of claim 14, wherein said article conducts light at at least one wavelength with an attenuation less than 200 dB/km.[956]

~~(a) placing into a polymerization container a sheathing solution comprising a sheathing polymerizable monomer and a sheathing dopant, the sheathing dopant having a refractive index lower than that of the polymer obtained by the~~[957]

~~polymerization of the sheathing monomer; and~~[958]

~~(b) causing the sheathing monomer of the sheathing solution to polymerize within the polymerization container in a cylindrical configuration to form a transparent sheathing tube.~~[959]

16. The ~~method~~[960] article[961] of ~~Claim 15~~[962] claim 1,[963] wherein the ~~material is in the~~[964] shape of ~~a~~[965] the article is an essentially[966] cylindrical ~~preform~~[967] rod.

~~17. The method of Claim 15 wherein the sheathing and core polymerizable monomers are different.~~[968]

17. The article of claim 16, wherein said rod is hot-drawn into a fiber that conducts light having a diameter less than said rod at a draw rate of at least 3 m/min.[969]

18. The ~~method of Claim 15 wherein the sheathing and core polymerizable monomers are the same~~[970] article of claim 1, wherein the shape of the article is an essentially cylindrical fiber having an outer diameter less than 1 millimeter[971].

~~26~~[972]

19. The ~~method~~[973] article[974] of ~~Claim 18~~[975] claim 1,[976] wherein ~~the~~[977] said sheathing polymer and said core polymer are formed from different[978] polymerizable ~~monomer is methyl methacrylate~~[979] monomers[980].

20. The ~~method~~[981] article[982] of ~~Claim 18~~[983] claim 1,[984] wherein ~~the~~[985] said sheathing polymer and said core polymer are formed from the same[986] polymerizable monomer ~~is 2,2-bis(trifluoromethyl)-4,5-difluoro-1,35 dioxole~~[987].

21. The article of claim 20, wherein the polymerizable monomer is methyl methacrylate.[988]

22. The article of claim 1, wherein said sheathing dopant is dimethyl sebatate.[989]

23. The article of claim 1, wherein said sheathing dopant is diisobutyl adipate.[990]

24. The article of claim 1, wherein said sheathing dopant is 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.[991]

25. The article of claim 1, wherein said sheathing dopant is diethyl succinate.[992]

26. The article of claim 8, wherein said core dopant is benzyl benzoate.[993]

27. The article of claim 8, wherein said sheathing dopant is dimethyl sebatate and said core dopant is benzyl benzoate.[994]

29. The article of claim 8, wherein said sheathing dopant is diisobutyl adipate and said core dopant is benzyl benzoate.[995]

30. The article of claim 8, wherein said sheathing dopant is 2,2,4-trimethyl-1,3-pentanediol diisobutyrate and said core dopant is benzyl benzoate.[996]

31. The article of claim 8, wherein said sheathing dopant is diethyl succinate and said core dopant is benzyl benzoate.[997]

32. A method for forming a gradient index plastic optical article comprising:[998]

(a) forming a tube of polymeric sheathing material that is at least partially transparent to light at least one wavelength from at least one polymerizable sheathing monomer including a sheathing dopant; and[999]

(b) forming a polymeric core that is at least partially transparent to light at at least one wavelength within the tube formed in step (a), with said core having a gradient in refractive index in a specific direction by:[1000]

(i) filling said tube with a composition including at least one polymerizable core monomer; and[1001]

(ii) polymerizing said core monomer.[1002]

33. The method of claim 32, wherein said tube of sheathing material is formed by:[1003]

(a) supplying a cylindrical polymerization container;[1004]

(b) placing a quantity of a composition including said at least one polymerizable sheathing monomer and said sheathing dopant into said container; and[1005]

(c) polymerizing said sheathing monomer to form a hollow polymeric tube.[1006]

34. The method of claim 32, wherein said sheathing dopant has a refractive index less than said polymerizable sheathing monomer when polymerized without the sheathing dopant.[1007]

35. The method of claim 32, wherein the composition in step (b)(i) further includes a core dopant.[1008]

36. The method of claim 35, wherein the core dopant has a refractive index greater than that of the polymerizable core monomer when polymerized without the core dopant.[1009]

37. The method of claim 32, wherein energy is supplied during step (b)(ii).[1010]

38. The method of claim 33, wherein energy is supplied during step (c).[1011]

39. The method of claim 37, wherein said energy is in the form of heat.[1012]

40. The method of claim 38, wherein said energy is in the form of heat.[1013]

41. The method of claim 33, wherein said polymerization container is rotated during step (c).[1014]

42. The method of claim 32, wherein said polymerizable sheathing monomer and said polymerizable core monomer are different.[1015]

43. The method of claim 32, wherein said polymerizable sheathing monomer and said polymerizable core monomer are the same.[1016]

44. The method of claim 43, wherein the polymerizable monomer is methyl methacrylate.[1017]

45. The method of claim 32 further comprising the step of hot-drawing the article formed after the completion of step (b) at a predetermined temperature and speed to form a gradient index optical fiber.[1018]

46. A gradient index plastic optical article having a polymeric sheathing that includes a sheathing dopant.[1019]

47. A gradient index plastic optical article comprising:[1020]

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer; and[1021]

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, including a core polymer and a specific overall concentration of a core dopant having a refractive index greater than that of the core polymer, said core dopant having a concentration gradient within the core in a specific direction;[1022]

said polymeric sheathing being constructed and arranged so that a difference in refractive indices between the central axis of said polymeric core, having said overall concentration of core dopant, and said polymeric sheathing exceeds a difference in refractive indices between said central axis of said polymeric core, having said overall concentration of core dopant, and said sheathing polymer.[1023]

48. The article of claim 47, wherein said overall concentration of core dopant is zero.[1024]

49. The article of claim 47, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.[1025]

50. The article of claim 47, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.[1026]

51. A gradient index plastic optical article comprising:[1027]

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer; and[1028]

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, comprising a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value, said core dopant having a concentration gradient within the core in a specific direction;[1029]

said polymeric sheathing being constructed and arranged so that the maximum service temperature of the article exceeds that of an equivalent article except having a sheathing comprised only of sheathing polymer and having a second overall core dopant concentration required to create a difference in refractive indices between the central axis of the core and the sheathing equal to said desired value.[1030]

52. The article of claim 51, wherein said overall concentration of core dopant is zero and where said polymeric core has a refractive index gradient within the core in a specific direction.[1031]

53. The article of claim 51, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.[1032]

54. The article of claim 51, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.[1033]

55. A gradient index plastic optical article comprising:[1034]

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, including a sheathing polymer ; and[1035]

a polymeric core coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, including a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a first overall concentration sufficient to create a difference in refractive indices between the central axis of the core and the sheathing of a desired value, said core dopant having a concentration gradient within the core in a specific direction;[1036]

said polymeric sheathing being constructed and arranged so that said light at at least one wavelength is conducted by the article with less attenuation than by an equivalent article except having a sheathing comprised only of sheathing polymer and having a second overall core dopant concentration

required to create a difference in refractive indices between the central axis of the core and the sheathing equal to said desired value.[1037]

56. The article of claim 55, wherein said overall concentration of core dopant is zero.[1038]

57. The article of claim 55, wherein said polymeric sheathing includes a sheathing dopant having a refractive less than that of said sheathing polymer.[1039]

58. The article of claim 55, wherein the refractive index at the central axis of said polymeric core is greater than the refractive index of said polymeric sheathing, where said article conducts light at at least one wavelength with an attenuation less than 500 dB/km.[1040]

59. A plastic optical preform article comprising:[1041]

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength and possesses a refractive index of a first value at said at least one wavelength, including a sheathing polymer and a plasticizer; and[1042]

a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer; said second value of refractive index exceeding said first value.[1043]

60. The article of claim 59, wherein the polymeric core has a refractive index gradient within the core in a specific direction.[1044]

61. The article of claim 59, wherein said preform can be formed into an essentially cylindrical optical fiber having an outer diameter less than 1 millimeter by extrusion.[1045]

62. The article of claim 61, wherein said fiber conducts light at at least one wavelength with an attenuation less than 500 dB/km.[1046]

63. The article of claim 59, wherein said preform can be formed into an essentially cylindrical optical fiber having an outer diameter less than 1 millimeter by hot-drawing.[1047]

64. The article of claim 63, wherein said fiber conducts light at at least one wavelength with an attenuation less than 500 dB/km.[1048]

65. The article of claim 64, wherein said fiber is hot-drawn from said rod at a drawing speed of at least 3 m/min.[1049]

66. The article of claim 64, wherein said fiber is hot-drawn from said rod at a drawing speed of at least 5 m/min.[1050]

~~21. The method of Claim 15, further comprising the step of: hot-drawing the graded index plastic optical material at a temperature and speed, to thereby obtain a graded index plastic optical fiber.~~[1051]

67. The article of claim 59, wherein said plasticizer acts as a sheathing dopant having a refractive index which is less than that of said sheathing polymer.[1052]

~~22. A graded index plastic optical fiber produced by the method of Claim 21 which is optionally jacketed with a suitable jacketing composition in either a single or duplex configuration.~~[1053]

68. The article of claim 59, when said polymeric core further includes a core dopant.[1054]

~~23. A tube of sheathing material comprising a sheathing~~[1055]
~~polymer and a sheathing dopant.~~[1056]

69. The article of claim 59, wherein said sheathing polymer and said core polymer are formed from the same polymerizable monomer.[1057]

70. The article of claim 69, wherein the polymerizable monomer is a perfluorinated monomer which yields an amorphous perfluorinated polymer upon polymerization.[1058]

71. The article of claim 59, wherein said sheathing polymer and said core polymer are formed from the different polymerizable monomers.[1059]

72. The article of claim 71, wherein the polymerizable monomer forming the sheathing polymer is a perfluorinated monomer which yields an amorphous perfluorinated polymer upon polymerization.[1060]

73. A method for making a gradient index plastic optical fiber comprising:[1061]
forming a polymeric preform rod comprising a polymeric sheathing and a polymeric core coaxially disposed within said sheathing, said polymeric core having a gradient in refractive index in a specific direction; and[1062]
hot-drawing said rod at a draw rate of at least 3 m/min into a fiber that conducts light of at least one wavelength with an attenuation less than 500 dB/km.[1063]

74. A plastic optical preform article comprising:[1064]
a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a first value at said at least one wavelength, and includes a sheathing polymer; and[1065]
a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer and a core dopant having a refractive index greater than that of the core polymer and present at a specified overall concentration;[1066]

said second value of refractive index exceeding said first value by at least 0.01 at said at least one wavelength, with said specified overall core dopant concentration not exceeding 12 %wt.[1067]

75. A plastic optical article comprising:[1068]

a polymeric sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a first value at said at least one wavelength, and includes a sheathing polymer; and[1069]

a polymeric core, coaxially disposed within said sheathing, which is at least partially transparent to light at at least one wavelength, possesses a refractive index of a second value at the central axis of the core at said at least one wavelength, and includes a core polymer and a core dopant having a refractive index greater than that of the core polymer;[1070]

said second value of refractive index exceeding said first value by at least 0.01 at said at least one wavelength, and the operating temperature of the article being at least 40 degrees C.[1071]

ABSTRACT ~~OF THE DISCLOSURE~~[1072]

~~Graded plastic~~[1073] Polymeric[1074] optical ~~materials~~[1075] articles[1076], including gradient index optical[1077] preforms and ~~fibers~~[1078] fiber[1079] produced therefrom, are described. Methods for producing the optical ~~materials~~[1080] articles[1081] using plasticizers and/or[1082] dopants in the sheathing of the ~~material~~[1083] articles[1084] are also described. ~~The graded~~[1085] Gradient[1086] index ~~plastic~~[1087] optical ~~materials~~[1088] articles made according to the invention[1089] have excellent optical characteristics, enhanced ~~flexibility~~[1090] mechanical properties[1091] and ~~good~~[1092] environmental stability, and enable more flexibility in the selection of materials.[1093]

??1??[1094]

??2??[1095]

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Split/Merged cell	
Padding cell	

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